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BIENNIAL REVIEW ON FLAME EMISSION, ATOMIC ABSORPTION, AND ATOMI--ETC(U)

FEB 78 G M HIEFTJE, T R COPELAND

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>A review of developments in flame emission, atomic absorption, and atomic fluorescence spectrometry is presented, and covers advances in instrumentation, theory, and methodology which have occurred over the period of Nov. 1, 1975-Nov. 1, 1977. Both English and foreign journals have been used in compiling an extensive bibliography. Coverage of published articles is critical rather than encyclopedic, and trends in the reviewed fields are noted.</p>		

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ERRATA

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- 79 line 28, "tetroganal" should read "tetragonal"
 lines 30 and 31, "ascrobic" should read "ascorbic"
- 80 line 24, insert "residence time" after "atom cloud"
- 81 line 9, "unto" should read "into"
 line 11, "nickle" should read "nickel"
 line 31, "for" should read "in"
- 82 line 9, insert "a solution of" between "using" and " Cu^{+2} ..."
 line 24, insert "cold-trap" between "with" and "collection"
 line 26 should read "to improve sample throughput rate."
- 83 line 34, insert a period after " 2700°C ." "CaOH" begins a new sentence.
- 85 line 28, "spectra" should read "spectral"
- 86 line 26 should read "For this limited range of excess interferent, the procedure worked well."
- 87 line 1, "AOAC" should be followed by "(Association of Official Analytical Chemists)"
- 88 line 1, "obsorption" should read "absorption"
 line 21, "overlap" should read "interferences"
 line 22, insert "monochromator by" between "the" and "landpass"
- 89 line 2, insert "Ni" between "the" and "signal"; "flawes" should read "flames"
 lines 5 and 6 should read "...to strongly affect its sensitivity; apparently (26F, 88F, 37F) Cr (III) is more ..."
 line 10, " $\text{Cr}_2\text{O}_4^{-2}$ " should read " CrO_4^{-2} "
 line 22, "manditory" should read "mandatory"
 line 27 should read "...temperature but strongly dependent..."
 line 31, insert "AA" between "(113F)" and "signals"
 lines 32 and 33 should read "...and H_3PO_4 . All interferences except Al were..."
 line 34, "action" should read "cation"
- 90 line 5, "nicelle" should read "micelle"
 line 8 should read "... and found Pt interferes with Pd, while Rh..."
- 91 line 6 should read "... dilution; the lowest Mg value for samples..."
 line 16 should read "...EDTA and analyzed by flame AA gave satisfactory..."
- 93 line 29, "was" should read "used"
 line 35, "bakgrounds" should read "backgrounds"
- 94 line 6, "gase" should read "gas"
 line 9, insert "(MECA)" between "analysis" and "has been"

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ERRATA, continued

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- 94 line 20, "chloroinated" should read "chlorinated"
line 21, "palced" should read "placed"
line 25, "unit" should read "emit"
lines 30-33, " T_iO " and " S_iO " should read " TiO " and " SiO "
- 95 line 2, "Allene" should read "Allen"

FLAME EMISSION, ATOMIC ABSORPTION, AND ATOMIC FLUORESCENCE SPECTROMETRY

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The present review covers books, articles, and chapters which appeared in the time period between November 1, 1975 and November 15, 1977. Unfortunately, because of the late arrival of some journals in our libraries, it was not possible to include all publications which appeared in November, 1977. It is hoped that these publications will be discussed in the next biennial review, and our apologies go to any authors whose recent work is not considered below.

Over 2500 publications dealing with the reviewed subject have appeared in the past two years, forcing us to reorganize this review somewhat and to restrict the scope of the material being covered. Specifically, we have elected for several reasons to omit completely any coverage of papers dealing primarily with applications of flame emission, atomic absorption, or atomic fluorescence spectrometry, and to dwell instead upon advances in theory, technique, and instrumentation pertinent to those fields. Although this move might not receive universal acclaim, we feel it can be readily justified on the following grounds. First, applications of analytical techniques are treated extensively in the biennial review of ANALYTICAL CHEMISTRY which appears on alternate years, the most recent of which was published in April, 1977. Second, applications of atomic spectrochemical analysis to particular problems can be readily located through Chemical Abstracts. Finally, information on applications of flame and other atomic spectrometric techniques are discussed extensively and evaluated critically in the excellent series Annual Reports on Analytical Atomic Spectroscopy published by the Chemical Society, located in Burlington House, London, W1V 0BN.

England (12A, 13A). Being produced annually, this review contains far more current information on applications than would be possible in a biennial issue. Furthermore, the greater length of the annual review permits a more encyclopedic and detailed discussion of topics than is possible here. As in previous issues, Volumes 5 and 6 of ARAAS, covering literature appearing in calendar years 1975 and 1976, respectively, are well-organized and contain a wealth of information. Both printed manuscripts and formal presentations are reviewed and critically evaluated, and trends in atomic spectrometry are noted and documented. The authors and editors of this excellent series are to be commended and readers of the present review are strongly urged to consult ARAAS for more detailed information about specific topics.

Even with restricted scope, it has been necessary to limit the number of articles being reviewed here, in order to provide a meaningful coverage. The criteria employed in choosing articles to be reviewed are similar to those set down in the previous issue (16A). These criteria are: 1) No paper was reviewed which largely duplicated another or incorporated only minor changes or innovations compared to an earlier publication. Included in this category are articles published in more than one language. For journals which appear in more than one language, reference is made, whenever possible, to the English version of the journal despite its ordinarily delayed date of appearance. In citing English translations, the year of appearance of the English volume has been employed, rather than the date of publication in the original language. When it has been necessary to cite an article appearing in a language other than English, every effort has been made to secure the Chemical Abstracts reference and include that along with the English translation in the Literature Cited. 2) Most papers published in the following analytical and physical journals have been reviewed -- Advances in High Temperature Chemistry, Analyst, Analytica Chimica Acta, Analytical Chemistry, Analytical

Letters, Applied Spectroscopy, Applied Spectroscopy Reviews, Atomic Absorption Newsletter, Critical Reviews in Analytical Chemistry, Critical Reviews in Environmental Control, Chemical Instrumentation, Combustion and Flame, High Temperature Science, Instruments and Experimental Techniques, Journal of Aerosol Science, Journal of Analytical Chemistry (USSR), Journal of Applied Spectroscopy (USSR), Journal of Chemical Education, Journal of the Optical Society of America, Optics and Spectroscopy (USSR), Optics Communication, Optik, Progress in High Temperature Physics and Chemistry, Review of Scientific Instruments, Spectrochimica Acta Part B, Spectroscopy Letters, Talanta, and Fresenius' Zeitschrift für Analytische Chemie. 3) No papers published in unreviewed journals have been considered. Included in this list are American Laboratory, Research and Development, Industrial Research, Laboratory Practice, Specs Speaker, Laser Focus, Optical Spectra, and other trade journals, free journals primarily used for advertisement, and magazines intended for consumption by the general public. 4) Only a few selected publications from journals other than those listed above in (2) have been reviewed. However, particularly innovative publications or those of fundamental importance have been reviewed, whatever their source. 5) As stated earlier, the emphasis in this review will be on flame spectrometry and on studies which deal with the devices intended to be direct replacements for a chemical flame as an atom cell. Thus, applications involving carbon or metal atomization systems will be reported while those utilizing electrical discharges or plasmas will not. By agreement, DC, radio-frequency, and microwave discharge sources will be reviewed in the section of this issue entitled Emission Spectrometry, authored by R. M. Barnes. Because of the increasing attractiveness of radio frequency-induced plasmas and

their similarity to chemical flames, readers are urged to consult the appropriate section of the review by Barnes.

The present review has been organized along lines similar to those employed before (16A). References have been grouped into six major sections, which have been divided along lines we feel will be most useful. These sections are: A. Reviews, Books, and Bibliographies; B. Fundamental Studies in Flames; C. Advances in Instrumentation; D. Electrothermal and Cold Vapor Atom Formation Devices; E. Developments in Technique and Procedure; F. Analytical Comparisons and Figures of Merit. References pertaining to each section have been listed in alphabetical order within each section and listed under Literature Cited.

Significantly, we have elected to assign a separate section to electrothermal and cold vapor atom formation devices in the present review, reflecting the increase in interest in these devices over the past two years. The high incidence of recognized matrix interferences with such devices is offset in many applications by their high sensitivity. Moreover, fundamental studies being directed at understanding the atom formation processes within electrothermal atomizers offer hope that such interferences might be overcome in the future. Until that time, however, it is our opinion that the chemical flame will remain the atom reservoir of choice for the majority of determinations employing atomic absorption or atomic fluorescence spectrometry. Other trends notable in the last two years are the growing interest in the development of new techniques and instrumentation for multi-element analysis and the emergence and acceptance of Zeeman modulation approaches to background-corrected, high-precision atomic absorption spectrometry. Accordingly, individual subsections of this review have been provided for each of these areas.

The most significant occurrence in the area of atomic spectroscopy during the past biennium has been the introduction and enthusiastic reception of commercial inductively coupled plasma torches for emission spectrometric analysis. Although such sources are not the subject of this review, their similarity and unavoidable comparison to chemical flames invites brief comment. In short, the ICP torch is relatively simple to use, provides extremely high sensitivity, low matrix interferences, and multi-element analysis capabilities for samples in solution. Consequently, in many ways it is clearly superior to the chemical flame. However, the ICP systems now available are extremely expensive (approximately \$10,000 for source alone), expensive to operate, bulky, and less convenient to operate than typical flame spectrometers. In addition, the ICP discharge generates extremely strong and highly structured background radiation, which requires a high dispersion, low scattered radiation spectrometer for accurate analyses. Finally, subtle interelement effects appear to exist within the ICP which are only now beginning to be appreciated and understood. Consequently, it is expected that ICP systems will find greatest use in laboratories where high sample throughput is imperative and where determination of at least five elements in each sample is required. In most other cases, the low cost and simplicity of atomic absorption instruments will secure their position in the analytical laboratory.

Reviews, Books, and Bibliographies

Trends and events of importance in analytical flame emission, atomic absorption, and atomic fluorescence spectrometry can be readily recognized from the proceedings of the important biennial International Conferences on Atomic Spectroscopy, and it has become a custom to report briefly on those conferences in this review. Interestingly, two such conferences were held in the past biennium and both were sponsored jointly with other organizations. The regularly scheduled International Conference on Atomic Spectroscopy (ICAS) was held in Prague, Czechoslovakia from August 8 to September 7, 1977. However, in honor of America's Bicentennial celebration, an additional conference was held in Philadelphia from November 15 through 19, 1976. Significantly, both these conferences combined ICAS with another important international spectroscopy conference, the Colloquium Spectroscopicum Internationale. Additionally, the Philadelphia meeting was co-hosted by the American-based Federation of Analytical Chemistry and Spectroscopy Societies.

Regrettably, the Philadelphia conference was considerably larger than most previous ICAS meetings and its theme far more diverse. Consequently, the impact of atomic spectroscopy was greatly diluted and the large number of parallel sessions necessitated missing several potentially important papers. Nonetheless, the overall quality of papers presented at the conference was high and their acceptance positive.

The conference in Czechoslovakia was more focused, although it also covered topics other than analytical atomic spectroscopy. The conference was unusual in its format in that it consisted of two parts. The first part, attended by all conferees, was held in Prague from August 30 to

September 3, 1977. In this principal part of the meeting, a large number of diverse topics was covered, including atomic spectroscopy and many other spectrometric methods. Following the principal congress, six special-topic "mini-symposia" were held at various locations throughout Czechoslovakia. Of greatest interest to individuals involved in atomic spectroscopy would be the symposia on "Optimization of Spectrochemical Methods," on "Spectrochemical Analysis of Metals", and on "Electrothermal Atomization Processes in Atomic Absorption Spectroscopy". In our view, this two-part format was highly effective and useful, and enabled conferees not only to broaden themselves by attending sessions outside their main area of interest, but also to focus later on specific topics in which they had more detailed interest.

Overall, both the principal congress and mini-symposia were well organized, located in settings conducive to scientific exchange, and well-attended by individuals from throughout the world. Invited lectures presented at the principal congress have been compiled in two volumes entitled "Proceedings of the XX Colloquium Spectroscopicum Internationale and 7th International Conference on Atomic Spectroscopy" and is available from the Czechoslovak Spectroscopic Society of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia. Unlike in most meetings, all plenary lectures were held on the same day, and were led by a talk by Sir Alan Walsh of CSIRO, Australia, on "Non-dispersive Systems in Atomic Spectroscopy." Walsh, who was recently knighted for his scientific contribution to the field of atomic spectroscopy, elaborated on a system first described in the previous ICAS in Melbourne in 1975. The system is extremely flexible and enables one to employ sputtering discharges or flames in a variety of ways,

including their use as primary sources of radiation, as atom cells for generating atomic vapor from sample material, or as resonance monochromators. Additional details concerning this system can be obtained from references cited in a later section. In another presentation, George Morrison of Cornell University underlined the importance of trace elements in biological materials and compared methods currently available for their analysis. His methods included atomic absorption spectrometry (AAS), electrothermal AAS, emission spectroscopy, inductively coupled plasma spectrometry, neutron activation analysis, spark source mass spectrometry, and X-ray fluorescence spectrometry. Morrison concluded that no single technique currently provides sufficiently high sensitivity for all elements now known to be important in biological systems. However, electrothermal atomization AAS provided the best compromise of high sensitivity, acceptable accuracy and precision, and low instrumental cost.

In the balance of the principal part of the congress, several trends seemed evident. One approach which seemed to gain momentum is the coupling of atomic absorption spectrometry and plasma spectrometry with separations techniques such as liquid and gas chromatography. Such a combination enables one to determine not only which elements are present in a sample but also to determine the state of such elements and in what compounds they are bound. Also, the entrenchment of electrothermal atomization techniques into atomic absorption was evident, as was the increasing acceptance of Zeeman-modulation techniques. Although atomic spectroscopists are becoming cognizant of the pitfalls of electrothermal atomization, the sensitivity, convenience, and small sample requirements of the technique override these objections in many cases.

Several books pertaining to or dealing with flame emission, atomic absorption, or atomic fluorescence spectrometry have appeared in the past two years. The third volume of the extremely useful series edited by J. A. Dean and T. C. Rains (7A) is now available and contains fourteen chapters covering the determination of 80 elements in matrices of various kinds. Important lines, sensitivities, detection limits, excitation conditions, interferences, separations and applications are provided. Unfortunately, very little information is presented on applications of electrothermal or other non-flame atomizations methods. However, electrothermal atomization is treated in detail in the text on that subject by C. W. Fuller (14A). Fuller treats both applications and theoretical aspects of these important atomizers, but emphasizes in his fundamental treatment only the vaporization and dissociation of oxides, making the treatment limited in its utility. In addition, many of the shortcomings of electrothermal methods are not carefully documented. An English edition of the book by Welz (42A) has been published and is substantially updated from the previous German version. The new text contains a thorough coverage of electrothermal atomizers, provides fundamental information on electrothermal atomization mechanisms and instrumental innovations and lists a number of applications of such devices. A new volume edited by Winefordner (47A) deals with atomic spectrochemical techniques from a very practical viewpoint and compares such techniques with others useful for trace analysis. The book is an excellent reference, useful for selection of methods to solve specific analytical problems. A basic textbook by Schrenk (31A) also discusses atomic spectroscopy but emphasizes optical emission techniques; only half of the book will be useful to flame spectroscopists. In addition, some of the instrumentation

which is presented is somewhat dated. Data compilations useful to atomic spectroscopists have been published by Robinson (28A) and by Meggers, Corliss, and Scribner (26A). The Robinson volume contains useful tables, including one listing band heads for molecules commonly found in flames and arranged by wavelength. Meggers, et al., have updated the earlier table of spectral line intensities published by the National Bureau of Standards and included 39,000 spectral lines which have been observed from flames and electrical discharges.

An interesting historical account of the impact of flame spectrometry on problem-solving was narrated by Betteridge (3A). Using flame emission techniques as an example, the narrative shows how analytical methods do not always arise in response to some specific need or problem, but are often developed independently and ahead of or parallel with theoretical concepts explaining them. The historical account by Burns (4A) is more detailed and of greater breadth, covering the entire scope of atomic spectroscopy. In contrast, the volume edited by Laitinen and Ewing (21A) reviews the entire history of analytical chemistry and enables one to place advances in atomic spectroscopy in a realistic perspective.

Still the most useful reviews in atomic spectroscopy are the "Annual Reports on Analytical Atomic Spectroscopy" (12A, 13A) which were mentioned earlier; every individual interested in this field is strongly advised to examine them. However, for an up-to-date categorized bibliography, readers are directed to the periodic compilation by Slavin and Lawrence (34A-37A).

Several reviews have included flame spectrometric methods in their overview of spectroscopic techniques. Among these are those by Elser (9A),

who emphasized instrumentation; by Fike, Frank, and Dreher (10A), who also considered high-temperature molecular spectroscopy; and by Klinkenberg (20A), who included nuclear methods. Winefordner (46A) also compared several analytical techniques, including atomic spectroscopy, while Veillon (39A) and Walker (41A) restricted their discussions to atomic methods.

Introductory treatments of atomic absorption spectrometry were prepared by Davis (6A), Lang (22A), and Williams (45A). The review by Aidarov (1A) served well to evaluate the present status of atomic absorption, but emphasized the utility of resonance detectors in new AA instrumentation. Reviews have begun appearing which emphasize furnace or chemical methods of atomization in atomic absorption. Included in this category are those by Massmann (24A), Shaw, Ottaway, and Littlejohn (32A), and Skudaeu, Shipitsin, and Morozov (33A). L'vov (23A) also provided an overview of the use of atomic absorption for the characterization of powders, while Gold'shtein and Yudelovich (15A) considered indirect atomic absorption methods for anion and non-metal determination.

Reviews dealing specifically with atomic fluorescence spectroscopy include those by West (44A), Razumov (27A), and Sanz-Medel, Perez-Bustamante, and Burriel-Marti (30A).

A number of reviews have dealt with the application of flame emission, atomic absorption, or atomic fluorescence to specific areas. The use of these techniques in clinical chemistry has been outlined by Dulka and Risby (8A), Caraway (5A), McGill and Kowalski (25A), and Fuchs, Dorne, and McIntosh (11A). Walker (40A) described how atomic absorption is employed in forensic science while Rubeska (29A) emphasized applications in geology. The overview by Welz (43A) included a number of industrial applications.

The use of standards is essential to the success of flame and furnace spectrometric techniques (indeed, to most areas of spectrochemical analysis). Consequently, the new gelatin trace-element reference material described by Anderson, Murphy, and White (2A) is welcome.

Also welcome is the exposition on nomenclature, symbols, units, and their usage in atomic spectroscopy published by IUPAC (17A-19A). We strongly endorse a more rigid definition of terms in spectrochemical analysis and support the substitution of the term "characteristic concentration" for the ambiguous word "sensitivity" frequently employed to designate the solution concentration which produces 1% absorption in AA.

Fundamental Studies

Most of the publications discussed in this section pertain directly to flame emission, atomic absorption, or atomic fluorescence spectrometry. However, others gleaned from physics or engineering literature have also been included when they contain information of fundamental importance or having potential practical application to analytical atomic spectrometry.

Nebulization, Desolvation, and Solute Vaporization. Lisienko, Muzgin, and Zolotavin (97B) investigated experimental parameters affecting droplet size distribution and sample transport efficiency for both peripheral and concentric pneumatic nebulizers and concluded that the concentric type was better. Furthermore, nebulization efficiency was improved by minimizing capillary wall thickness and maintaining as small a distance as possible between the capillary tip and concentric air port. Strangely, Fainerman (33B) found that a concentric nebulizer operated at subsonic nebulizing gas flow

velocities was not strongly affected by the location of the nebulizer tube. In their study on the mechanism of ultrasonic nebulization, Bassett and Bright (11B) emphasized that droplet formation from liquid jets is similar, no matter whether the disruptive energy be supplied pneumatically or ultrasonically. Using high-speed motion pictures, they observed capillary waves on the surface of the disrupted liquid and the development of bubbles within it, indicating that both cavitation and wave formation contributed to the spray formation. Muzgin, Grigor'ev, and Pupyshev (124B) also studied ultrasonic nebulization and ascertained that approximately 90% of the generated spray consisted of droplets less than 8 μm in diameter, if the ultrasonic driving frequency was approximately 3 MHz. Electrostatic spraying was examined by Buraev and Vereshchagin (21B), who noted that spraying quality deteriorated as the conductivity of the liquid being nebulized increased. From this observation, it would appear that electrostatic spraying has little future in analytical flame spectrometry.

Enhancement of flame spectrometric signals through use of organic solvents is well known. Szivos, Polos, and Pungor (158B) examined this process in detail and attribute the observed signal increase to both improvements in aspiration rate and reduction in droplet size for the organic solvent. Routh and Denton (146B) separated these factors by use of an ultrasonic nebulizer and observed a signal enhancement in a reducing acetylene flame that was due principally to increased nebulization rate. In lean flames, an additional enhancement arises for some elements through addition of reducing species to the flame.

It has long been known that droplets of a combustible solvent burn irregularly for a short period after ignition. Law (92B) has concluded

that droplet heating is the source of this instability, and in a later study (93B) calculated that the instability would be much the same, no matter whether convective or conductive heat transport within the droplet was controlling. Conveniently, under conditions expected in flame spectrometry, no significant departure from the expected constant rate of droplet surface contraction is expected. Raghunandan and Mukunda (157B) corrected for changing thermal conductivity and heat capacity in the medium surrounding evaporating droplets and obtained closer agreement with theory. Aqueous droplets containing dissolved solutes (NaCl and CaCl_2 mixtures) evaporate more slowly than pure water droplets, according to Golli, Arnaud, Bricard, and Treiner (44B), and the difference can be ascribed to solute-solvent interactions. For very small charged droplets (less than 10^{-6} cm), ions can actually separate or "evaporate" from the droplet as it desolvates. Such a process might be important in flame spectrometry, since droplets are always charged during pneumatic nebulization. However, such small droplets could only be produced upon evaporation of fairly low-solute solutions.

The change in mass and volume of an aerosol droplet as it evaporates in an analytical flame influences the velocity of the droplet within the flame, as shown theoretically by Boss and Hieftje (16B) and by Li (95B). The decreasing droplet volume reduces the upward force exerted on the droplet by flowing flame gases, whereas reduced droplet mass lowers the opposing gravitational force; the overall result is a more rapid increase in droplet velocity than predicted by earlier models involving constant droplet size. From these calculations, droplets are moving essentially at the flame gas velocity by the time desolvation is complete; consequently,

the remaining particles reside in an essentially quiescent environment, a situation which markedly affects their vaporization. Ghosh and Natarajan (42B) also examined the effect of droplet evaporation on its velocity.

Droplet sizes and their velocities can both be measured with a new rotating-mirror technique devised by Tolfo and Standt (161B). In the new method, a stroboscopic photograph of droplets is obtained, enabling their measurement; velocities were determined by blurring of droplet images. Webster, Weight, and Archenold (169B) employed holography to obtain instantaneous droplet size determinations within a flame. Spectral filtering of the laser radiation eliminated interference from flame background, enabling droplets as small as several μm to be seen. We assume it would also be possible to double-pulse the laser to obtain a double-exposure hologram. Droplet velocities could then be determined from the displacement of individual droplets during the interval between pulses.

Advances in technique for the measurement of submicron particles will greatly aid the determination of particle vaporization mechanisms in flame spectrometry. Mallove and Hinds (115B) have devised a new instrument which employs both differential sedimentation and light scattering in a specially designed centrifuge to enable the measurement of particle sizes below 5 μm . Schwartz and Andres (151B) have constructed a time-of-flight aerosol spectrometer suitable for flame sampling and sensitive to particles below 1 μm . A helium-neon laser and silicon photodiode array were employed by Knollenberg (86B) to obtain both size and shape information on aerosol particles having diameters between 1 and 10,000 μm . Refinements in theory for determining particle sizes through light scattering were announced by Heller and Nakagaki (64B), Penner, Bernard, and Jerskey (132B), and Roth,

Gebhart, and Heigwer (145B).

Paule (129B) noted that the rate of evaporation of Al_2O_3 particles increases discontinuously when the particle melts. Through detailed investigations, Paule determined that the particle evaporation coefficients remain constant, but that particle emissivity increases discontinuously upon its fusion, causing a rapid temperature jump and increased vaporization of the particle at that time. If emissivity changes indeed affect particle vaporization to such a degree, one wonders whether the phenomenon could not be employed to advantage in flame spectrometry and also to what extent the intense background from some highly efficient flames enhances particle volatilization.

Atom Formation and Distribution. An excellent series of articles by L'vov and his coworkers (102B-111B) has now been translated into English. The first three manuscripts in the series (102B-104B) considered the production and distribution of atoms along flames supported on slot burners. Models were proposed and developed that predict the cross-sectional distribution of particle aerosols in a long-path flame. Because this distribution is dependent on the particle size, the authors point out that all factors should be held constant which affect particle size in conventional atomic absorption spectrometry. In particular, standards and samples should both have volatile matrices whenever possible, and should not contain species that form complexes with the analyte. In an extension of their model, the authors also show that final atom concentration at any point in a slot flame depends on matrix volatility, the diffusion coefficient of the atoms, and the flame gas velocity. This model is used to explain "lateral diffusion interference" effects and can be employed in a simple scheme for measuring

atomic diffusion coefficients in hot gases. In communications 4 and 6 of their series (105B, 107B), these workers consider flame temperatures and composition and their effect on atom formation. Elaborate calculations were performed to determine temperatures and equilibrium compositions of nitrous oxide-acetylene and air-acetylene flames. One of the interesting findings is that neither flame should contain ultraviolet-absorbing species when it is fuel rich. Also, a new method for flame temperature measurement was proposed which is based on the measurement of the absorption of two spectral lines from a narrow band (hollow cathode-like) source. Because the method relies on absorption rather than emission, it describes a temperature related to differences in lower rather than higher energy level populations. Consequently, the measured temperatures are more likely to approach true kinetic temperatures. Also, the approach is applicable to sooty, luminous, and high or low temperature flames. Simplified equations useful for temperature determination using Sn or Fe lines are presented.

Communications 5, 7, 8, and 10 (106B, 108B, 109B, 111B) of L'vov's series deal specifically with atomization processes and their effects upon analytical results in flame spectrometry. Communications 5 and 8 (106B, 109B) clarify the anomalous atomization behavior of Sn in hydrogen-based and hydrocarbon flames. Through examination of Sn volatilization in acetylene and hydrogen flames, in furnace-flame devices, and in furnaces alone, the workers show experimentally that the surprisingly low sensitivity for Sn in cool hydrocarbon flames (such as air-acetylene) is due to the formation of difficult-to-volatilize Sn carbides. These data agree with thermodynamic calculations and previously reported data. Moreover, this hypothesis successfully explains the hitherto confusing reduction of Sn absorption

by organic solvents in hydrogen flames, the better sensitivity for Sn in hydrogen than in acetylene flames, and the relatively high temperature (2500 K) required for Sn atomization in a graphite furnace.

Communication 7 (108B) addressed the effects of flame richness and anion character on the volatilization of Ni, Mn, Co, and Fe. Indirect evidence suggests that anion interference occurs during vaporization rather than through gas-phase interactions. Also, under extremely fuel-rich conditions, nitrates or sulfates of these metals form carbides, an undesirable occurrence which can be avoided through use of non-reducible salts such as chlorides. Communication 10 (111B) predicts the influence of such interference effects on curvature of analytical plots. Curvature can be expressed as a function of the ratio between solute particle diameter and the distance it travels before vaporizing.

Katskov, Kruglikova, L'vov, and Polzik (83B) examined the atomization of several elements in a low-temperature hydrogen flame to which acetylene had been added, and found a signal reduction for many elements, suggesting strongly the formation of gaseous carbides. In contrast, Yoshimura and Morimoto (171B) added carbon-black powder to an air-acetylene flame and found that it could eliminate interferences on Al and Ti caused by fluoride and phosphate ions. Sturgeon and Chakrabarti (157B) studied flame absorption profiles of molybdenum and its oxides as a function of complexing agents, solvents, and stoichiometry and attributed their findings to carbide formation. However, their observed upward shift in maximum absorbance with increasing acetylene flow rates might also have been caused by reduction of the common thermally-formed oxide MoO_3 to the less volatile solid Mo metal. Unfortunately, the workers did not obtain a temperature profile

of their flame, so it is impossible to confirm or disprove their hypothesis. In a more detailed investigation, Rubeska (147B) suggested that the effect of Al on other elements (V and Mo) can be ascribed to its preventing their reduction from the oxide to the less volatile metal. Thus, the presence of Al in a matrix will enhance the volatilization of Mo by scavenging reducing species and preventing the formation of solid Mo. This would be another explanation for the enhancement effects previously dubbed "lateral diffusion interferences."

A careful study of atom formation in air-acetylene flames was performed by Halls (47B, 48B) who compared spatial variations in atom concentration with localized temperatures and concentration gradients of reducing species intrinsic to the flame. Hydrogen radicals exhibit similar behavior to that of some elements (principally In), suggesting their involvement in atomization. In addition, Halls related free energies of reduction of several metal oxides to the free energies of oxidation of reducing flame species and suggested that C_2 and H radicals can be credited with most of the reducing power of the air-acetylene flame. However, if kinetic limitations exist, more powerful reducing species (e.g., C atoms or CH radicals) might also play a part. This hypothesis is not inconsistent with the widely-held view of atom formation involving the dissociation equilibrium of metal oxides; however, it suggests that controlling equilibria might involve flame species. Like Halls, Nakahara and Musha (125B) attributed In atomization in cool H_2 flames to the decomposition of InH , whose formation is in turn enhanced by the presence of Mg halides. Li (94B) outlined a preliminary but potentially very useful model for atom formation in analytical flames. In this model, parameters

for droplet size distributions, droplet desolvation rates, particle vaporization rates, and atomic diffusion coefficients are included, but would have to be obtained experimentally or from other sources. Stochastic variables are introduced to enable droplet size to vary and the paths of different species to change with respect to each other. Although the model assumes simplified atomization processes and does not consider interactions among droplets, particles, and vapor-phase products, it provides a convenient bridge between atom concentration profiles which can be measured and fundamental theories predicting atom formation from individual droplets.

Ubhayakar (162B) proposed a model to describe the volatilization of a combustible solid particle in an oxidizing atmosphere, while Simonova, Raikhbaum, and Drovov (154B) determined the effect of size and composition of particles in a solid aerosol on the signal produced when they are blown into a plasma. Raikhbaum, Erkovich, and Malykh (220C) considered the influence of atomization efficiency and rate, diffusion kinetics, and optical geometry on curvature of analytical plots in atomic absorption spectrometry. Although useful, the model is somewhat limited in that it neglects ionization effects and assumes a cylindrical flame. Todorovic, Vukanovic, Simic, and Peric (160B) described the use of high-speed cinematography and cross-correlation of photomultiplier signals to obtain transport velocities of particles in a plasma; presumably, the techniques would be equally useful for investigations in flames.

The thermodynamics of volatilization, dissociation, and atomization of metals and their oxides were studied by several groups. Nemets and Nikolaev (126B) determined the concentration and saturation vapor pressure at various temperatures of Cr, Mn, and Fe, whereas Wagoner and Hirth (168B)

examined the vaporization kinetics of NaCl. Kordis and Gingerich (88B), Srivastava (155B), and Farber and Srivastava (34B) published dissociation energies of rare earth and alkaline earth oxides. Ashton and Hayhurst (5B) extended their series of determinations of diffusion coefficients in flames to calcium hydroxide, strontium hydroxide, barium hydroxide, and copper.

Ionization in Flames. A semi-empirical model for computing ion concentrations in premixed hydrocarbon flames was offered by Ay, Ong, and Sichel (6B). The model considers the kinetics of ion formation, ambipolar diffusion, and convection, but requires knowledge of the flame kinetics. Miller, Newman, and Page (118B) have continued their work involving ionization associated with solid particles in flames to reveal that electrostatic probes inserted in the flame can actually induce ionization themselves, through interaction with the particles. Because the presence of a particle seemed necessary to induce the probe error, most measurements in analytical flames should be accurate, unless they are taken very low in the flame, where particulate species might reside. Gussak and Semenov (46B) studied the temperature and ionization spatial profiles in a laminar air-hydrogen flame front and concluded that chemi-ionization dominated ion formation. A new method for measuring electron concentrations in flames and plasmas was reported by Razmadze, Chkuaseli, and Gol'Dinov (139B). The method employs an argon ion laser and three-mirror interferometer and is capable of 1 μ s time resolution.

Radiational Excitation and Radiational or Non-radiational Deactivation in Flames. Lovett and Parsons (100B) described a new method for

calculating optical collision cross-sections and Voigt a parameters which compare well with measured values for elements not having significant hyperfine structure. Cross-sections and a parameters were tabulated for 114 transitions of 52 elements in an air-acetylene flame, and procedures were presented for converting the a values to those corresponding to other flames or other temperatures. Kozlov (90B) published a new technique for determining absolute values of oscillator strengths of atoms through measurement of the absorption of two spectral lines. Collisionally-induced energy transfer between excited Na atoms was investigated by Allegrini, Alaetta, Kopystynska, Moi, and Orriols (2B). A continuous-wave laser, tuned to either of the Na D lines, was found to induce atomic fluorescence from a host of spectral lines, some of which had energies greater than twice that of the D line. Apparently, collisions between two excited Na atoms yield one ground state and one highly excited atom, the latter of which then emits; the difference in energy between the fluorescent and excitation photons is supplied from or converted to translational energy.

The development of extremely narrow-band, high-stability tunable lasers has made it possible to measure fundamental atomic parameters to an accuracy previously impossible. The reader interested in the new procedures developed using such lasers is referred to a section on "Tunable Lasers" in the Advances in Instrumentation portion of this review. In the present section, some of the fundamental parameters measured with lasers are reviewed.

In addition to their monochromaticity, lasers can provide extremely intense electromagnetic fields over very short time periods. The shift of atomic energy levels under the influence of such intense fields was examined by Gersten and Mittleman (41B). Also, quantum beats and transition

rates between energy levels in a multilevel atom under the influence of laser radiation was studied by Agarwal (1B).

Perhaps of greatest fundamental interest to atomic spectroscopists is the laser's ability to provide definitive values for excited state lifetimes of atoms, for from such values can be derived their reciprocals (the Einstein A coefficient) and absolute values of oscillator strengths. Knowledge of such parameters is essential to the feasibility of developing absolute methods of atomic spectrometry. Carlson, et al. (23B) and Feinberg, et al. (35B) described methods for such measurements. In addition, Phillips (133B) and Knight and Milonni (85B) considered deviations from exponential decay and errors which might arise in lifetime measurements of atomic states because of such processes as radiation trapping. Other workers who measured specific excited-state lifetimes are compiled in Table 1. Interested readers are directed to the original literature for information concerning methods of measurement and the particular transition of each element under investigation.

Collisional quenching by foreign species usually shortens excited-state lifetimes experienced by an atom in a flame below those values cited in Table 1. In fact, quantum yields in both fluorescence and emission measurements are limited by such quenching processes, making the measurement of quenching kinetics important analytically. Hannaford and Lowe (49B) have determined the rare-gas pressure dependence of the intensities of boron fluorescence at two different spectral lines and concluded that rare-gas quenching was responsible for their observations. Marek and Niemax (116B) quantitatively determined the influence of xenon atom collisions on the lifetime of atomic cesium states. Quenching measurements were extended

to a flame environment by Jansen, Hollander, and Van Helvoort (78B) in their determination of quenching cross-sections for excited strontium. Unfortunately, the flame which was employed ($\text{CO}/\text{N}_2\text{O}$) is not widely used analytically. The influence of different atmospheres on atomic fluorescence intensity was ascertained by Karyakin, Belyaev, and Koveshnikova (82B), who concluded that O_2 and CO_2 are the most significant quenching gases in the atmospheres employed in most analytical atom cells (flames, electrothermal atomizers, etc.). Hertel, Hofmann, and Rost (63B) investigated polarization effects in the quenching of excited Na atoms by diatomic molecules while Kopeikina and Yanson (87B) examined a sort of "inverse" quenching involving energy transfer from excited Na molecules to Na and K atoms. Quenching rates of Bi, Sn, Hg, and rare earth atoms, respectively, were measured by Bevan and Husain (13B), Foo, Wiesenfeld, Yuen, and Husain (38B), Phillips (134B), and Penkin and Komarovsky (131B).

Spectral Line Profiles and Their Effect on Working Curves. The accurate measurement of spectral line profiles has received a substantial amount of attention over the past two years. Bradberry and Vaughan (17B) described how a new, multi-pass Fabry-Perot interferometer could be employed to measure extremely narrow line widths. The multi-pass instrument exhibits a band pass shape which falls off much more rapidly than the Airy function common to single-pass interferometers, enabling accurate measurement of spectral line wings. The method requires prior knowledge of the spectral line shape, however. Vasconcellos (165B) reviewed the theory of one-photon high-resolution absorption spectroscopy while Olivero and Longbothum (128B) and Pierluissi, Vanderwood, and Gomez (135B) outlined

techniques for calculating and fitting Voigt line profiles. Blass (15B) used the power spectrum of a Gaussian line and the Nyquist theorem to set down proper sampling criteria to be employed in digitizing a spectrum or spectral line, while Horlick and Yuen (67B) showed how spaces between such sampled data could be filled in using a Fourier-transform approach. An accurate deconvolution technique for determining line intensities and half-widths was proposed by Chang and Shaw (24B), whereas Gold, Rechsteiner, and Buck (43B) published an algorithm which enables sequential spectral stripping from a complex spectrum. Unfortunately, self-absorption generates substantial errors in the proposed method, limiting its use in atomic spectroscopy. Nemets, Nikolaev, and Flisyuk (127B) compared Voigt a parameters which were determined from narrow-line absorption and total (integrated) absorption techniques. Values so obtained were employed to calculate optical diameters for broadening collisions and also absolute atomic concentrations. A didactically useful approach to converting atomic line widths from frequencies to wave lengths and vice versa was described by Lovett and Parsons (99B). Jansen, Hollander, and Aikemade (76B, 77B) performed a number of measurements on atomic spectral line profiles in flames. Using a pressure-scanned Fabry-Perot interferometer, the self-absorbed profile of a Sr line was determined as a function of atom concentration; observed line widths (FWHM) agreed well with those calculated from the Voigt expression and Beer's law. Significantly, half-widths which would be found under optically thin conditions could be determined through extrapolation of those obtained at higher concentrations, where signal-to-noise is good but self-absorption contributes to broadening. These same workers employed optically thin atomic concentrations and similar

instrumentation to compare half-widths and spectral shifts of absorption and emission core profiles of Ba and Sr resonance lines. Because both elements behaved similarly and their line shapes were consistent with the Maxwell-Boltzmann equilibrium, the observed radiation was judged to be thermal in origin. Spectral line wings of Na and Sr resonance lines were also examined by the Utrecht workers, but satellite-like features precluded close agreement with theoretical predictions. Van Dijk (163B) also examined the wings of the Na resonance lines, but used a narrow-band tunable dye laser for the measurement. By measuring the fluorescent signal as the laser's wavelength was scanned, he obtained an excitation profile which was examined for contributions from multi-photon absorption. Because of the extremely low probability of such events and their large spectral separation from the measured line (more than 100 \AA), they can be safely expected to be insignificant in practical flame spectrometry.

Dönszelmann and Neijzen (29B) and Grove, Wu, and Ezekiel (45B) examined spectra under conditions of intense irradiation, such as would be produced by a laser. Higgins (65B) and Fleurier, Sahal-Brechot, and Chapelle (37B) studied the effect of Stark broadening on atomic spectral lines. The effects of radiative and collisional broadening on line emission in a laser-produced atomic plume were investigated by Apruzese, Davis, and Whitney (4B).

L'vov, Polzik, Katskov, and Kruglikova (112B) employed a pressure-scanning Fabry-Perot interferometer to measure the shift in spectral lines which occurs in flames compared to those emitted by hollow cathode lamps.

The shifts so measured gave excellent agreement with theory. L'vov (110B) included the effects of such shifts in his review on the causes of Beer's Law plot curvature in atomic absorption. The influence of source line width, its asymmetry and hyperfine structure in the source and absorber lines were also considered. Wagenaar and de Galan (167B) used a similar technique to measure hollow cathode lamp spectral profiles and determined the lamp's temperature from their results. Deviations from Beer's law caused by line shape differences between the primary light source and absorber were considered by Davis and McFarlane (28B). Often, an empirical correction factor is included in the Beer's law relationship to overcome these deviations; unless such a factor is experimentally determined to be essentially constant under the measurement conditions, its use should be avoided. The influence of spectral line profiles on curves of growth was examined through computer simulation by Jansen and Hollander (75B). Such curves, which are log-log plots of the spectrally integrated absorption factor vs atom density, were expected to be affected somewhat by the shape of the spectral line wing which, as indicated above, does not always follow Voigt behavior. Fortunately, the departure from predictions is expected to be experimentally insignificant and fundamental parameters determined from curves of growth should be valid.

Characteristics of Flames. Several new flames have been proposed and evaluated for use in analytical atomic spectroscopy. Johnson and Winefordner (79B) replaced the nitrogen ordinarily present in an air-acetylene flame with argon, to yield a flame which exhibits higher quantum efficiencies. Shielding the flame with flowing argon and eliminating the highly

quenching nitrogen improved both detection limits and working curve linearity; moreover, flame temperature and fuel-to-oxidant ratio could be independently controlled through variation of the three flame support gas flows. Similar advantages were reported by Saturday and Hieftje (148B) for a flame comprised of helium, oxygen, and acetylene. In addition, the use of helium rather than argon or nitrogen as a flame gas diluent increased flame gas thermal conductivity and improved atom formation efficiencies. The He-O₂-C₂H₂ flame emits a relatively low spectral background and exhibits a temperature near that of the N₂O-C₂H₂ flame. A natural gas flame was coupled with a chamber electrode-flame atomizer by Razumov (140B) to yield a system which produced extremely low atomic absorption and atomic fluorescence detection limits for elements of high volatility.

The combustion mechanism in low-pressure acetylene-oxygen flames was investigated by Vandooren and Van Tiggelen (164B) and by Basevich, Kogarko, and Posvyanskii (10B). The mechanism of propagation, which is similar to that operating in a CH₄-O₂ flame, involves the successive oxidation of C₂H₂ through an attack by hydroxyl radicals and oxidation by oxygen. The reaction mechanism of a H₂-N₂O flame was examined by Balakhnine, Vandooren, and Van Tiggelen (7B), who reported a number of important reaction steps and their rate constants, notably that involving decomposition of N₂O into nitrogen and oxygen. Burdett and Hayhurst (22B) showed that the nitrosyl ion and neutral nitric oxide are in extremely rapid equilibrium in both acetylene-air and hydrogen-air flames. Lovachev (98B) assessed the importance of vortex formation on flame propagation while Andrews, Bradley, and Lwakabamba (3B) examined the applicability of theories of turbulence

to the structure of turbulent flames. The highly important Reynold's number seems to be correlated in turbulent flames with the ratio of turbulent flame velocity to laminar burning velocity. Vermeulen, Danilowich, Heydlauff, and Price (166B) showed that a flame can either attenuate or amplify an acoustic wave, depending on the strength of the wave and its frequency. Amplification, if it occurs, can result either from flame front modulation or from induced vortex entrainment of oxygen into the reacting flame mixture. Markstein (117B) measured radiative energy transfer from turbulent diffusion flames and concluded that such flames cannot be regarded simply as laminar flames of greater optical depth.

Determining the composition of combustion flames continues to be an active area of research. Rasmuson, Fassel, and Kniseley (138B) corrected the concentrations of natural flame species in N_2O/C_2H_2 flames which they earlier calculated and obtained slightly improved agreement with experimental findings. Apparently, an erroneous value for the formation constant for CO_2 had been employed in the earlier investigation. Kosaka, Asahina, and Hayashi (89B) employed a thermodynamic model of the C_2H_2/N_2O flame to calculate equilibrium partial pressures of intrinsic flame species; free atom fractions were then computed for several elements as a function of fuel-to-oxidant ratio and water content of the flame; values so obtained agreed well with experimental results. According to Müller-Dethlefs and Schlader (123B), water acts not only as an inert diluent in a flame, but inhibits carbon formation and produces greater heat release. Thus, flame temperature and burning velocity do not decrease as rapidly with added water as would otherwise be expected. Hayhurst and coworkers (59B, 60B, 62B) critically discussed the sampling of ions from atmospheric pressure flames for

mass spectral identification. Their system was characterized, its influence on the flame during sampling was assessed, and the validity of the generated mass spectra discussed. Mueller, Boltendahl, and Roertgen (120B, 121B) measured nitrogen oxides and oxygen concentrations in an air-acetylene flame. Hanson, Kuntz, and Kruger (50B) showed how a tunable diode infrared laser spectrometer could be employed to obtain high-resolution absorption spectra of intrinsic flame species, while Jones and Mackie (80B) evaluated the use of C_2 resonance fluorescence as a technique for measuring transient flame events. C_2 concentrations in oxygen-acetylene flames were also measured by Baronavski and McDonald (8B, 9B) in two rather similar publications. The perturbation of high-voltage electrostatic probes on a flame was examined by Bradley and Ibrahim (18B). Raman spectroscopic measurement of intrinsic flame species has become feasible with recent instrumental advances and was reported by Lapp and Penney (91B) and by Mueller, Klainer, and Miller (122B).

Background spectra in atomic spectroscopy can be generated by either molecules or atoms and by species naturally present in a flame or by those added with a sample. Consequently, high-resolution spectra of such species are useful. Haraguchi and Fuwa (51B) published atomic and molecular absorption spectra for indium which occur in an air-acetylene flame, while Brown and Ginter (19B) obtained an absorption spectrum of Ag. Fluorescence of $CaOH$, $SrOH$, and $BaCl$ molecular fragments in flames was reported by Human and Zeegers (68B). According to Furuta, Yoshimura, Nemoto, Haraguchi, and Fuwa (39B), hyperfine structure appears in the absorption spectrum of Na halides in an air-acetylene flame because of molecular dissociation. The high-resolution infrared emission spectrum of OH radicals in an oxyacetylene flame was analyzed by Maillard, Chauville, and Mantz (114B).

A number of new techniques have been proposed and old methods criticized for the determination of temperatures in flames and other high-temperature gases. The two-line absorption method outlined by L'vov and co-workers (107B) was discussed in the section of this review dealing with atom formation in flames. A similar approach was taken by Ide, Yanagisawa, Kitagawa, and Takeuchi (71B) in the determination of temperatures above a glassy carbon strip atomizer, a tantalum filament atomizing device, and in an air-acetylene flame. An atomic fluorescence method for flame temperature determination was employed for local sensing by Haraguchi, Smith, Weeks, Johnson, and Winefordner (52B) and by Benetti, Omenetto, and Rossi (12B). The method, which was suggested earlier by several authors, employs the relative intensities of Stokes and anti-Stokes spectral lines of a chosen element to obtain values for flame temperatures. Because the exciting and fluorescent radiation can be directed and detected at 90° from each other, spatially localized temperatures can be measured without the use of an Abel inversion. Because non-resonance fluorescence must be used, probe elements employed as thermometric species must have three utilizable energy levels; In, Ga, and Tl have been found to be most useful, with Tl providing better results for high-temperature flames (>2000 K) and In proving optimal at lower temperatures (700 K - 2600 K). Haraguchi and Winefordner have applied the technique to the measurement of local temperatures in air-acetylene (54B) and air-hydrogen (55B) flames and, with coauthor Weeks, in H_2 -Ar (entrained air) flames (53B).

If a flame is not in local thermodynamic equilibrium, it is necessary to determine not only electronic excitation temperatures, but also rotational, vibrational, ionization, and other temperatures to characterize

it completely. Vibrational and rotational temperatures of flames were obtained by Drake and Rosenblatt (30B) and Stricker (156B) using laser Raman spectroscopy. Like the atomic fluorescence method described above, the Raman approach is capable of providing localized temperature readings, particularly if the exciting laser is focused. Moya, Druet, and Taran (119B) obtained similar results using coherent anti-Stokes Raman scattering, whereas Robben (143B) demonstrated that Rayleigh scattering could yield even more precise temperatures than the Raman method. Maclatchy and Miner (113B) employed a Langmuir probe and the Saha equation to measure ionization temperatures in a flame, while thermal temperatures were obtained by Ivashchenko, Korobchenko, and Bondarenko (74B) through capacitive transducer measurement of electron (Johnson) noise in an oxyacetylene flame. Lueck and Mueller (101B) utilized a narrow-band, frequency-doubled CW tunable laser to scan across an OH ultraviolet rotational line and obtained both the rotational temperature of that species and its concentration.

Reif, Fassel, and Kniseley (142B) showed that flame excitation temperatures could be obtained without a calibrated reference light source. In their method, a non-calibrated tungsten lamp is set to the same temperature as the flame by a two-step procedure involving first a line-reversal adjustment followed by a reduction in lamp brightness temperature in accordance with the emissivity of the lamp filament. After these initial adjustments, the true lamp temperature is the same as that of the flame. Next, measurements of the emission intensity of a chosen element are made at spectral lines whose transition probabilities are known; simultaneously, measurements of the intensity of the adjusted tungsten lamp are taken at the same wavelengths. Finally, Wien's law describing the wavelength dependence of an emitting black body is employed to derive a complex function

which, when coupled with the measured values, can be plotted against the lower energy level of the spectral lines which were employed. The slope of this plot yields the desired temperature, whose value agrees well with those obtained using other methods. Reif, Fassel, and Kniseley (141B) also emphasized the importance of accurate transition probabilities when the slope or two-line method of spectroscopic temperature determination is employed. Errors as large as 150 K can arise through transition probability errors. Other errors in flame temperature measurement, deriving from cold boundary layers in the observed region, were cited by Daily and Kruger (27B). Hayhurst and Kittelson (61B) employed electrically heated thermocouples of Ir and of Ir/Rh to determine flame temperatures below 2400 K. Interestingly, they also found it possible to determine the flame's thermal conductivity by measuring the heat transfer coefficient between the flame gases and thermocouple wire as the wire's diameter was changed. Users of the method are cautioned that uncoated thermocouple wires can undergo catalytic heating, especially in the reaction zone of hydrogen flames, where radical concentrations are high.

A detailed appraisal of Abel inversion methods for spatially resolved spectroscopic measurements was published by Scheeline and Walters (150B); these same authors described algorithms for implementing the inversion (149B). The influence of temporal and spatial inhomogeneity, optical alignment, and depth of field distortion were all examined and, unless controlled, were found to generate significant error. Rogoff (144B) described a clever optical system for an automatic Abel inversion in a cylindrically symmetrical radiating medium. Pitz, Cattolica, Robben, and Talbot (136B) employed Rayleigh scattering measurements to determine temperature and density in a hydrogen-air flame.

Both vertical and swirl gas velocities in flames were measured using a laser Doppler anemometry technique developed by Chigier and Dvorak (25B). With the new technique, which is based on optical heterodyning, localized velocities can be determined without the necessity of disturbing the flame or inserting probes into it. Vertical flame velocities were determined by Cox (26B) through use of two thermocouples spaced a known vertical distance within the flame. Random localized thermal variations, propagating upward with the flame gases, then induced similar variations in the output of each thermocouple. Cross-correlation of the electrical signals from the two thermocouples then enables the determination of the temporal displacement of the thermocouples and a resultant evaluation of flame velocity. Schlieren techniques, widely used to evaluate flame or plasma homogeneity and laminarity, can be rendered far more sensitive if the illuminating source is tuned to the edge of a resonance line of a species within the flame. Such an approach was utilized by Siebeneck, Koopman, and Cobble (153B), who seeded a plasma with barium atoms and tuned an exciting dye laser to the edge of a barium ion line; improvements in sensitivity of 100-1000X were claimed.

The frequency distribution of noise present in a number of primary sources, plasmas, and flames was reported by Talmi, Crosmun, and Larson (159B). Noise spectra from most sources were similar, exhibiting $1/f$ character at low frequencies and appearing "white" elsewhere. However, certain flames supported on Meker burners possessed high frequency peaks which were attributed to organ-pipe oscillations within the burner top. In addition, unexpected structure in the spectrum of noise from a turbulent flame was ascribed to either the aspiration system or to desolvation/

vaporization processes. In a later exchange, Ingle and Talmi (72B) disagreed whether flicker noise was emphasized sufficiently in the earlier noise source investigation. Liddell (96B) examined fluctuations in an atomic absorption signal which exist when no analyte is present. Under such conditions, which should hold near the detection limit for analytical determinations, dominant noise sources were found to be photon noise, lamp flicker, and variations in flame transmission. Pealat, Bailly, and Taran (130B) examined noise in turbulent flames using Raman measurement of N_2 density fluctuations.

An electric field, generated by potentials in the kilovolt range, can increase the propagation rate of an alkane-air flame, according to a study by Yachkov, Polonskii, and Klimov (170B). Apparently, the electric field accelerates positive ions within the flame, which in turn enhances combustion through mechanical disturbance of the flame front. Kimura and Ogiwara (84B) examined the influence of a magnetic field on an air-propane flame which had been augmented with a 1.2 KW electrical discharge. The magnetic field seemed to aid in dispersion of the electrical discharge energy throughout the flame but caused undesirable spirals in the flowing charged gas stream.

Advances in Instrumentation

In this section, publications will be reviewed which deal primarily with new instrumentation designed for, or applicable to, flame emission, atomic absorption, and atomic fluorescence spectrometry. We have attempted to divide the papers into categories dealing with specific instrumental components; however, because many papers deal with several aspects of a

spectrometric system, some overlap is expected. Therefore, readers interested in a thorough coverage of any specific component are urged to examine all categories.

Nebulizers and Burners. Perhaps the most novel new technique for nebulizing sample solutions was introduced by Dresner (71C) and employed a device termed a "Babington nebulizer". In this device, the nebulizing gas is passed into a hollow sphere in whose surface exists a small hole or slot. The liquid to be nebulized is merely allowed to flow over the outer surface of the sphere, past the hole or slot, and is thereby disrupted into a fine aerosol. Required air operating pressure is in the range of 5 to 20 psi common to flame spectrometry and a droplet size range between 2 and 50 μm is produced. Application of the Babington system to analytical flame spectrometry was reported by Fry and Denton (92C). In a dramatic demonstration, it was shown possible to nebulize liquids ranging from medium-weight oil to undiluted tomato paste and to pass the resulting aerosol directly into a flame. Although pulpy or fibrous samples (such as tomato paste) were found to separate somewhat in the aerosol stage, the more fluid portions of even such samples were carried efficiently into the source and useful analytical determinations could be made on them. From initial accounts, the "Babington" nebulizer would seem to offer substantial promise for the analysis of difficult samples in flame spectrometry. An ultrasonic nebulizer contained entirely within the base of a laminar-flow burner was devised by Suddendorf, Gutzler, and Denton (258C) and used to introduce microvolumes of sample solution reproducibly into the flame. The most useful sample volumes were found to be in the range of 25-100 μl , although volumes as large as 300 μl could be employed if improved concentration detection limits were needed.

Branched pneumatic nebulizer capillary tubes for sample introduction were explored by a number of workers for different reasons. Fuller (94C) inserted samples into one arm of the capillary and standard solutions into the other to simplify standard addition determinations; in addition, inter-element interferences were found to be easily examined by introducing inter-ferents into the second capillary branch. In contrast, Miller and Edwards (190C) showed that interferences could be overcome by adding releasing agents through a second capillary and mixing them with sample solution within the dip tube itself. Goulden (103C) showed that required sample solution volumes could be reduced by injecting air into the sample capillary dip tube through a side arm. In this way, the magnitude and duration of the signal could be increased and samples as small as 25 μ l could be employed. A branched sample-introduction capillary was also employed by Tse, Wong, and Wong (276C) to combine a sample contained in an organic solvent with an aqueous-based standard solution. Not unexpectedly, an error of up to 20% resulted from this procedure, presumably because inorganic salt standards do not volatilize exactly as their organic counterparts. A conventional burner was modified for use with organic liquid fuels by Singhal and Banerjee (242C), simply by branching the nebulizer tube and introducing the organic fuel in one arm. Fuller (93C) found that stable slurries could be formed from finely-ground oxides by dispersing them in a 0.005% Na hexametaphosphate solution; the slurries could then be nebulized directly. Fuller and Thompson (95C) mixed thixotropic and defoaming agents into the same kind of slurry and found that the resulting suspensions would be stable for several days. Obviously, the resulting highly viscous sample would be more amenable to analysis in an electrothermal atomizer than in a flame. By adding a small amount of surfactant followed by brief sonication, Thompson and

Godden (269C) were able to directly nebulize samples of whole blood.

A comprehensive theoretical study of factors affecting the performance of pneumatic nebulizers was published by Heinemann (124C). Nebulizer geometry, capillary diameter, support gas pressure and its stability, solution viscosity and temperature fluctuations were all considered in the analysis. According to Rudnevskii, Demarin, Molyanov, and Sklemina (232C), the optimum temperature for heated desolvation chambers is 250° C for aqueous samples, 160° C if methyl isobutyl ketone is employed, and 220° C for isoamyl alcohol samples. With the proper desolvation chamber temperature, signals can be increased as much as twenty-fold. Reischl, John, and Devor (226C) found that the charge acquired by aerosol droplets as they are pneumatically generated can be neutralized by opposite inductive charging, simply by surrounding the nebulizer tip with an inert electrode maintained at a high potential.

Stupar (257C) introduced a new long-path burner for use with either air-acetylene or nitrous oxide-acetylene mixtures. Flame gases exit the burner through two parallel slots, between which are ports through which the sample aerosol is carried by flowing argon; aerosol is supplied from a 3 MHz ultrasonic nebulizer. Advantages claimed for the new burner are reduced complications from lateral diffusion interferences, a reduction in flame background, a richer reducing environment to aid in atom formation, and the ability to handle increased sample volumes. Kono (164C) also devised a multiple-slot flame, but employed his two outer slots to "sandwich" the air-acetylene flame issuing from a central slot between two sheets of flowing oxygen. The design appeared especially useful when organic solvents are employed and was claimed to provide a higher flame

temperature. One wonders what the temperature gradient in such a flame might be. Thompson and Godden (268C) slightly widened the slot in their nitrous oxide-acetylene burner top and employed pulse nebulization to minimize clogging when highly concentrated (10% weight/volume) samples were introduced. Their flame was also diluted with nitrogen to avoid flashback problems. An empirical expression derived by Maekawa (182C) describes the effect of channel length on flame quenching in a rectangular port such as found in a slot burner. Heated absorption tubes, coupled with cool flames, were utilized by Uchida and Iida (277C) and by Iida and Uchida (138C); the latter study marks the first time an indirect (chamber) nebulizer has been employed with an absorption tube.

Solid or Novel Sample-Introduction Techniques and Microsampling Procedures. Publications discussed in this section emphasize sample introduction into flames. However, some devices are used by themselves and the interested reader is referred to the later section on electrothermal and other non-flame atomization approaches. Reviews covering methods for direct solid sample atomization were prepared by Langmyhr (173C) and Razumov (223C). The thesis by Bath (12C) dealt with similar material. The review by L'vov (178C) emphasized methods for analysis of powders.

Lord, McLaren, and Wheeler (176C) freeze-dried biological samples, diluted them with naphthalene, pressed them into pellets, and atomized them directly in an electrothermal system. Marks, Welcher, and Spellman (184C) utilized a similar approach to determine several metals in milled chips of complex alloys. As in most solid sampling procedures, it was necessary to employ specially fabricated standards which were similar

in composition to samples. An induction furnace was used by Thomassen, Solberg, and Hanssen (267C) to atomize air particulate samples collected on a filter paper. Gough (102C) modified a sputtering chamber to permit the direct analysis of metals in alloys; the new system provides higher atomic densities and permits more convenient measurements using atomic absorption. McDonald (187C) added internal standards to samples atomized in a sputtering chamber to correct for variations in sputtering rate. As a result, a single set of standards could be utilized for the analysis of alloys and powdered metallic and non-metallic samples. The versatile sample position mechanism described by Chaban and Hagstrum (41C) would prove quite useful in such sputtering chambers.

In the "boat method" for solid sample determination in flame spectrometry, samples are held within the flame on a convenient support material and allowed to atomize slowly. This technique was critically evaluated by Orlov, Pobedonostev, and Savel'ev (202C). The effect of flame temperature, boat thickness, its composition and height in the flame, and the effect of fuel richness above the boat were all examined. Apparently, the boat casts a "shadow" in the flame, to produce a carbon-rich atmosphere above it, thereby increasing the incidence of carbide formation and reducing atom formation efficiency.

The most common method for introduction of microsamples into flames still involves the application of the sample to a refractory support followed by insertion of the support into a flame. A review and assessment of the problems associated with this technique was published by Vogel and Hartley (287C). Shapkina and Prudnikov (237C) and Kubota, Golightly, and Mavrodineanu (167C) found platinum-based alloy wires to be a suitable

support medium for samples of relatively volatile elements. In contrast, Kahl, Mitchell, Kaufman, and Aldous (147C) showed that a wider range of elements could be determined if the support were a microsampling cup constructed of Mo metal and inserted into an N_2O/C_2H_2 flame. To minimize oxidation of the Mo cup and thereby extend its lifetime and reduce non-specific absorption by Mo oxides, the cup was allowed to cool in a special container sheathed with nitrogen. The stainless steel burner employed with the Mo cup system is also worthy of note, since it was designed for flashback prevention and enclosed an unusually small volume of premixed combustible gases. Prudnikov and Shapkina (216C) inserted a resistively heated pyrolytic graphite filament into a N_2O/C_2H_2 flame to obtain a sample support which could be raised to the sublimation temperature of graphite in a one-second period. Extremely high sensitivity and impressive precision resulted. The same "furnace-in-flame" approach was compared by Prudnikov and Shapkina (217C) to a simple platinum wire introduction method in an air-acetylene flame. Best results were obtained by using low flame gas flows and by carefully selecting the region above the sample support where measurements were taken. Prudnikov (214C) extended the same technique by employing a two-stage burner. A lower "needle" flame aids in volatilizing the sample from the electrically heated graphite atomizer inserted into it; additional gas entry ports higher in the flame form a more reducing environment and provide better excitation. Extremely impressive detection limits were cited. The "furnace-in-flame" technique was compared to several competitive microsampling approaches by Prudnikov, Kalachev, and Shapkina (215C) and it was concluded that sensitivity and range of application are best for electrothermally heated graphite cuvettes

in argon. In contrast, the simplest device was an electrothermally heated graphite rod or cuvette operated in air. Volatile elements can be easily determined simply by introducing them into a flame on an inert support while oxidizable or refractory elements are best measured with a furnace-in-flame method or with an argon-surrounded, electrically heated graphite cuvette. Skudaev, Shipitsin, and Morozov (244C) adjusted the flame velocity around an electrically heated graphite rod to minimize turbulence. Also, the rod configuration enabled larger sample volumes to be employed, thereby increasing concentration sensitivity. With these modifications, precision and detection limits were comparable to those cited for conventional electrothermal atomization, but non-specific absorption was substantially reduced and difficult-to-analyze samples could be handled more easily. Razumov (225C) sealed samples into a hollow graphite tube fashioned from a spectrographic electrode and heated the tube resistively while it was supported in a natural gas flame. Volatilized sample atoms then diffuse slowly through the walls of the electrode into the flame, where they are observed by atomic absorption or fluorescence. Because of the low flame rise velocity, atoms reside in the observation region longer, and provide larger signals. Moreover, solids and viscous liquids can be handled with ease. In a later publication, Razumov (224C) empirically determined optimal experimental conditions for use with the chamber electrode atomizer.

Eagle and Orren (73C) reproducibly nebulized sub-milliliter volumes of sample solution into a flame merely by briefly dipping the nebulizer tube into the desired sample. Peak integration was found to provide highest precision. Inglis and Nicholls (139C) described a simple sample injection valve for the introduction of sample microvolumes.

A dc arc discharge, mounted outside the flame, was employed to atomize solid samples, powders, and liquids by Kantor, Fodor, Youssef, and Pungor (149C). Similarly, Dorofeev, Mikhailov, Razyapov, and Chupakhin (70C) employed an interrupted arc between carbon electrodes for atomization. Sample solution sprayed into the arc produced atomic absorption calibration curves which were linear over three orders of magnitude. A high-voltage spark served as a solid sample atomizer feeding a flame in the device of Human, Scott, Oakes, and West (135C), but rather long pre-spark times were required for the generation of stable signals. Induction heating of samples yielded high sensitivity for mercury determination in the atomic absorption measurements of Kuwae, Hasegawa, and Shono (171C). McCullough and Vickers (186C) directed the atomic vapor from a tantalum filament vaporizer up the nebulizer tube of a conventional atomic absorption burner system. Not only could microsamples be utilized, but the device exhibited relative freedom from non-specific absorption effects.

Because of the success enjoyed by the inductively coupled plasma torch in emission spectroscopy, it is not surprising to see it employed as an atom reservoir for absorption and fluorescence as well. Montaser and Fassel (192C) showed that cadmium, zinc, and mercury yield even higher atomic fluorescence than atomic emission signals from such a torch if an electrodeless discharge lamp supplies the primary radiation. The inductively coupled plasma torch designed by Mermet and Trassy (188C) is intended specifically for use in atomic absorption. Plasma gases enter the torch from the side while the bottom has been removed to enable resonance radiation to be directed down the rather lengthy plasma bore and thereby provide higher sensitivity. A theoretical evaluation of the utility of

high-temperature plasma atomizers in atomic absorption was forwarded by Korovin (165C). Belyaev, Tatsii, Vnukevskaya, and Makarova (15C) observed both emission and absorption from a combined flame-arc discharge. Located within the flame, the arc served both as sample atomizer and emission source, whereas absorption was observed higher in the flame, where arc background was minimized. Lau, Held, and Stephens (174C) collected atoms on a water-cooled silica tube placed within an air-acetylene flame. After a sufficient number of atoms were trapped, they were released to provide a much larger signal. Sensitivities, trapping efficiencies, and atomization kinetics of the device were evaluated for several elements.

High-power lasers are still being investigated as potential atomization devices for atomic absorption and fluorescence spectrometry. It has been found possible to vaporize solids, liquids, powders, and slurries and the resulting vapor has alternatively been observed directly or been swept into long-path tubes or flames. Regardless, sensitivity remains mediocre, interferences are frequent, and precision is marginal. Laser atomizers have been investigated by Ishizuka, Uwamino, and Sunahara (140C), Kantor, Polos, Fodor, and Pungor (150C), Diggle, Gehring, and MacFarlane (66C), Sukhov, Zalotukhin, and Ziyabkina (259C), and by Vul'fson, Gribovskaya, Karyakin, and Yanushkevich (288C). Matousek and Orr (185C) enclosed their sample in a graphite tubular furnace and irradiated it with a pulsed CO₂ laser. The furnace not only controls initial temperature and confines the laser plume to a desired region, but provides a well-defined atom cell and controls the absorbing light path precisely. Koenig and Neumann (157C) directed the beam of a continuous-wave ion laser back and forth across their sample in a raster pattern to allow spatial profiling of sample concentrations with a resolution of 0.008 mm².

Primary Sources for Atomic Absorption and Atomic Fluorescence. Hollow Cathode Lamps. A useful review on hollow cathode discharges oriented toward their application as spectrochemical emission sources was prepared by Slevin and Harrison (247C). Bevan and Kirkbright (21C) evaluated the influence of fill-gas pressure, cathode temperature, and discharge current on the spectral profile of the Ca 4226.7 Å resonance line in a demountable hollow cathode lamp. Apparently, Doppler effects and self-absorption are the only significant causes of broadening in such a source and these are minimized by water cooling of the cathode and continuous purging of fill gas. Zhechev, Dyulgerova, and Angelova (308C) showed that spectral line shape and width vary radially across a hollow cathode discharge. Zhechev, Dyulgerova, and Pacheva (307C) also obtained high-resolution scans of emission lines from hollow cathode lamps.

The thesis by Kuo (169C) explored programmed high-current hollow cathode lamps in analytical spectroscopy. Also, Kabanova and Sautina (146C) found less noise in atomic absorption measurements performed with a pulsed hollow cathode lamp. Not unexpectedly, lamp pulsing is most helpful for weak emission lines and when high-temperature atom cells are employed. Johnson, Mann, and Vickers (145C) employed a computer-controlled power supply and a simplex algorithm to ascertain optimal conditions for operating hollow cathode lamps in a pulsed mode. Plots were presented showing the influence of selected variables (peak current, pulse width, and continuous dc level) on both peak and integrated lamp intensity as other variables were held at their optimal level. More detail on these experiments is found in the thesis by Johnson (144C). Caroli, Milazzo, and Benincasa (38C) proved the hollow cathode source to be more stable than either a

glow discharge lamp or a spark light source. Theoretical and experimental determinations of rare-gas ion and metastable atom concentrations and excitation mechanisms in hollow cathode lamps are discussed in the papers by Djulgerova, Jechev, Pacheva, and Rashev (67C), Kojadinovic and Ricard (163C), and Ferreira and Delcroix (82C, 83C).

Electrodeless Discharge Lamps. Bazhov and Zherebenko (13C) attempted to explain the oscillatory instability exhibited by some electrodeless discharge lamps (EDLs) constructed using metal halides. Their hypothesis is that vaporized intact halide molecules or molecular fragments scavenge electrons, leading to a relaxation from the conventional ring-type discharge to a glow. In the glow mode, the discharge is concentrated to regions of greatest electrical field, so that the lamp walls cool, causing molecular species to condense on them. As a result, electron scavenging is reduced and the discharge returns back to the conventional mode, which increases wall temperature and causes the cycle to repeat itself. The instability can apparently be overcome by adding metals to the lamp which form stable gaseous halides having a low electron affinity. Bentley and Parsons (17C) described the preparation of EDLs from volatile covalent hydrides of several metals; further details are available in the thesis by Bentley (16C). Barnett, Vollmer, and Denuzzo (10C) evaluated commercial EDL sources and found them to be far more intense than similar hollow cathode lamps. Childs and Schrenk (47C) examined different fill materials, inert gases, pressures, and temperatures for the preparation of sulfur EDLs with greatest intensity and stability. The best lamps were prepared using S or H₂S with He, Ne, or Ar at 0.1-0.2 torr. Commercial EDLs were applied to atomic fluorescence spectrometry by Ullman, Favez, and Winefordner (278C).

and found to produce no better detection limits than a 300 W eimac lamp. Drift was cited as the most serious drawback of the commercial EDLs. Gabriel (97C) described a new resonant cavity for use with EDLs which provides a high voltage field for auto-ignition of the lamp. A flexible, efficient slab-line cavity for the excitation of EDLs was devised by Hammond and Outred (112C). Castleden and Kirkbright (39C) determined both line profiles and spatial intensity distributions for Pb electrodeless discharge lamps; line intensity appears to be greatest just inside the tube wall and decreases to about $1/3$ its maximum value at the tube center. Kuramochi, Matsuo, Matsuda, and Fukuyo (170C) measured spectral profiles of an isotopically pure Rb EDL.

Spectral Continua and Other Sources. Johnson, Fowler, and Winefordner (143C) compared a pulsed and continuous-wave eimac continuum xenon lamp in their abilities to excite atomic fluorescence. Surprisingly, the two were found to be comparable, primarily due to the instability of the pulsed lamp and its large required dc operating current. In contrast, Boutilier, Bradshaw, Weeks, and Winefordner (28C) showed that pulsed sources, coupled with gated detection systems, should produce superior signal-to-noise ratios for non-resonance atomic fluorescence. Moreover, if time-resolution techniques can be employed with the pulsed source, even resonance-line fluorescence measurements should be superior to those obtainable with a dc source. Unfortunately, few present sources can be pulsed on a time scale which would permit resolution of atomic fluorescence from background scattering signals. Hopefully, this limitation will be overcome with the development of new laser-based sources. Cochran and Hieftje (52C) examined the spectral and noise characteristics of an eimac arc lamp and showed that

much of the lamp's instability arises from thermally-produced turbulence above the arc. Consequently, blocking that portion of the lamp's reflector results in a lowered signal but an improved S/N ratio. Image quality of the arc within the eimac lamp was found to be far inferior to that produced by conventional short-arc xenon lamps, making the eimac device less desirable when a point-source is needed. Talmi, Crosmun, and Larson (265C) published noise spectra of several other primary sources used in atomic spectrometry. The thesis by Brinkman (30C) explores the use of exploding wires as continuum excitation sources for atomic fluorescence spectrometry. Popov and Aleksandrov (213C) devised a circuit useful for supplying and modulating the power to gas discharge lamps.

Omenetto, Boutilier, Weeks, Smith, and Winefordner (200C) investigated the surprisingly low signal-to-noise improvement which has been reported for pulsed-source atomic fluorescence spectrometry. The reasons for such low gain are different for various sources. Pulsed hollow cathode lamps must produce a peak radiance 100-1000 times that of a continuous-wave lamp to provide equivalent signal-to-noise ratios because of the duty factor involved. Self-reversal in pulsed hollow cathode lamps aggravates this situation. In contrast, pulsing a xenon arc lamp produces a change in spectral distribution and lamp efficiency drops. Laser sources are plagued with multimode operation when they are pulsed and are limited in their utility by saturation of atomic energy levels. Consequently, greatest gain will be obtained with laser sources when high saturation powers are required (e.g., for UV lines) and when quenching is severe.

Tunable Lasers. Despite earlier indications of the impracticality of tunable lasers in analytical atomic spectroscopy, applications of such

sources continue to increase, and several new techniques employing tunable lasers have been developed. Moreover, the ability of such lasers to provide important fundamental information on atoms and their interaction with radiation has generated an enormous number of papers in the physics literature. We will not attempt here to cover exhaustively the fundamental information which has been obtained with lasers over the last biennium. However, we hope to indicate the scope of laser applications and assess the importance of lasers to future work in atomic spectrochemical analysis.

Walther (292C) has prepared a review dealing with both fundamental and practical applications of tunable lasers to atomic spectroscopy; in contrast, Steinfeld's (254C) review is broader, covering additional applications of lasers to analytical chemistry. The proceedings of a conference concerning tunable lasers and their application was published by Mooradian, Jaeger, and Stokseth (193C). The two-part series by Green (104C, 105C) is didactically oriented and provides a useful introduction to dye laser instrumentation, whereas the review of Querry (219C) covers applications in spectroscopy of such lasers.

A versatile nitrogen-pumped tunable dye laser capable of being computer controlled is described and characterized in the thesis by Harrington (121C). A similar system, controlled by a microprocessor, was developed by Perry, Bryant, and Malmstadt (206C). Yamagishi and Szabo (301C) incorporated a piezoelectric drive for both the grating and etalon in their tunable dye laser, making the system capable of being accurately tuned electronically. The innovation by Hanna, Kärkkäinen, and Wyatt (113C) eliminates the complex and delicate beam-expanding telescope which is employed in many dye lasers to reduce output bandwidth. To expand the beam, radiation from a dye

cell is directed at near grazing incidence to a prism, which refracts and expands the beam, which then passes to a grating. The intricacies of frequency doubling, which practically limit much of the potential routine application of tunable lasers to atomic spectroscopy, were rendered simpler and fully automatic by Saikan (233C). In his system, a frequency-doubling crystal is employed, but is neither angle- nor temperature-tuned. Rather, the angle of incidence of laser radiation upon the crystal is controlled by means of an automatically rotated dispersing element (prism or grating); rapid scanning of the resulting second-harmonic radiation from 230-350 nm is possible. Defreese and Malmstadt (64C) devised a dual-beam dual-detector ratio measurement system capable of 10 ns resolution and useful for correction of pulse-to-pulse variations in short laser bursts. The problem of locking a tunable laser's output wavelength to that of a desired atomic transition can be accomplished with the systems described by Meyer (189C), Yabuzaki, Endo, Kitano, and Ogawa (300C), Man, Cerez, Brillet, and Hartmann (183C), and Endo, Yabuzaki, Kitano, Sato, and Ogawa (75C).

Omenetto (199C) critically appraised the advantages and limitations of pulsed excitation sources, including lasers, for exciting atomic fluorescence. The review on laser fluorimetry by Zare (306C) was broader, but indicated several areas of application in atomic spectroscopy. Smith, Blackburn, and Winefordner (249C) partially overcame the disadvantage of a limited tunable range exhibited by CW dye lasers by employing non-resonance transitions. Impressive detection limits were cited for Na and Ba in air-acetylene and $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flames. Green, Travis, and Keller (107C) also measured Na and Ba using a CW laser, but in a $\text{H}_2-\text{O}_2-\text{Ar}$ flame. Measurements of scatter and noise from their flame as a function of excitation

power led them to claim that signal-to-noise ratios increase little beyond laser powers of 10 W, making high-power pulsed lasers of limited utility. On the contrary, we feel that the small accessible wavelength range of CW lasers and their high rate of dye consumption, coupled with the ability of pulsed lasers to saturate atomic transitions and permit non-resonance line detection, combine to render pulsed lasers optimal at present. Alkemade and Wijchers (3C) also take Green, et al., to task by indicating that a dip seen in the center of a measured spectral line might not have been self-reversal, as claimed, but was perhaps a result of unintentional spatial masking of the flame. Smith, Winefordner, and Omenetto (248C) were able to saturate Na in an air-acetylene flame at an incident radiant power density of 10^{13} W/cm² nm, provided by a CW dye laser. Under saturated conditions, Na concentration profiles were measured in two flames with a spatial resolution of 0.01 cm. Other CW dye laser experiments in atomic spectroscopy were performed by Walther (291C).

Brod and Yeung (31C) coupled a flash lamp-pumped dye laser and a long-path Na cell to experimentally verify a theoretical expression for pre-filter effects. Sharp and Goldwasser (239C) also measured Na in a vapor cell with a flash-pumped dye laser, but compared radiant powers necessary to saturate the 589 nm transition with those calculated from an expression derived from conventional rate equations. An attempt was made to explain the substantial disparity on the basis of coherent superradiant processes. A direct-line transition enabled Hohimer and Hargis (128C) to obtain a 20 pg/ml detection limit for Cs atomized by a non-flame device. An electrothermal atomizer was coupled with a powerful pulsed laser by Bolshov, Zybin, Zybina, Koloshnikov, and Majorov (25C) for the measurement of Fe and Pb. Sub-picogram

detection limits were obtained and an impressive eight-decade linear working curve was claimed. Baronavski and McDonald (11C) mapped C_2 concentrations and obtained excited-state quenching rates in an O_2/C_2H_2 flame, employing a dye laser and saturated excitation.

The thesis by Olivares (65C) explored a number of aspects of tunable-laser-excited atomic fluorescence spectrometry, including saturation, the determination of excitation spectra, the measurement of excited-state lifetimes, the influence of radiation trapping on atomic fluorescence signals, and the analytical utility of saturated atomic fluorescence spectrometry. Particularly useful is a new kinetic theory describing the saturation of atomic energy levels with a laser of short pulse duration and the establishment of proper experimental conditions for verifying the theory. Daily (59C, 60C) also indicated the analytical advantages of energy-level saturation and formulated a rate equation to describe excitation and saturation by a transient radiation pulse. Omenetto, Winefordner, and Alkemade (201C) derived an expression for the atomic fluorescence and thermal emission intensity under saturated and near-saturated conditions, when various amounts of self-absorption are present. Photon anti-bunching, which can occur when atoms are excited by a brief radiation pulse, could affect measurements made with tunable lasers and was explored by Kimble, Dagenais, and Mandel (155C). Sobolewska (250C) explored how the fluorescence spectrum of a two-level or three-level atom would be affected by excitation with an intense, monochromatic beam. Other publications dealing with the influence of transient laser pulses on the absorption and fluorescence spectra and saturation behavior of atoms are those by Avan and Cohen-Tannoudji (7C), Badalyan, Dabagyan, and Movsesyan (8C),

Cohen-Tannoudji and Reynaud (53C), and Driver and Snider (72C).

The sensitivity of atomic absorption can be greatly increased if the atoms are measured within the cavity of a tunable laser. Intracavity absorption has been reviewed by Stepanov and Rubinov (255C) and a determination of specific elements using the technique has been reported by Burakov, Misakov, Nechaev, and Yankovskii (35C), Maeda, Ishitsuka, Matsumoto, and Miyazoe (180C, 181C), Traeger, Neumann, and Kowalski (275C), and Takubo (264C). Tohma (273C) and Belokon and Rubinov (14C) presented theoretical treatments of the intracavity absorption process and considered the influence of mode competition and spatial relaxation within the laser on the sensitivity of such measurements. Antonov, Koloshnikov, and Mironenko (4C) suggested a modulation technique for increasing the sensitivity of intracavity measurements.

A new approach to elemental analysis employing tunable lasers has been described by Green, Keller, Schenck, Travis, and Luther (106C) and dubbed the "opto-galvanic effect". Actually, the effect operates by photo-enhanced thermal ionization of individual atoms. In operation, the current passing between two electrodes held in or near a flame is measured while the electrodes are held at constant potential with respect to each other. When a species residing in the flame is excited by an incident laser beam, its degree of thermal ionization is slightly increased, leading to a change in the measured current. Lock-in amplifier detection of the ac current resulting from a modulated laser helps overcome background current from residual ionization. The technique appears sensitive and is claimed to be simpler to implement than conventional laser spectroscopy. However, it would seem that spectral and ionization interferences

would still be extremely troublesome. The opto-galvanic effect was employed by King, Schenck, Smyth, and Travis (156C) to calibrate a tunable laser output wavelength and bandwidth by scanning the laser's wavelength and monitoring the current passing through an irradiated hollow cathode lamp.

Gelbwachs, Klein, and Wessel (99C) combined saturated absorption and non-resonance fluorescence to achieve extremely high sensitivity detection of Na (to 10 atoms/cm^3). However, the ultimate detection limit (a single atom) was reported by Hurst, Nayfeh, and Young (137C). Their technique consisted of laser-induced resonance ionization of the desired atom followed by conventional ion detection. High-resolution laser spectroscopy of lanthanide ion spectra provides the basis for a sensitive, selective method for the measurement of species in solids, according to Gustafson and Wright (109C). Because the high-resolution splitting in the measured spectra reflects the environment of the lanthanide, the method is able to discern the identity and concentration of other, non-fluorescent ions which lie in proximity to the lanthanide in the solid matrix (298C).

Several exciting new techniques for the measurement of Doppler-free spectra of atoms have been developed using lasers and are described in reviews by H~~ä~~nsch (114C, 115C), Walther (291C), and Bloembergen and Levenson (24C). Well-written accounts of specific techniques were published by Feinberg, H~~ä~~nsch, Schawlow, Teets, and Wieman (80C) using laser polarization spectroscopy; by Kaminsky, Hawkins, Kowalski, and Schawlow (148C) with modulated lower-level population spectroscopy; and by Griffith, Isaak, New, Ralls, and Van Zyl (108C) using heterodyne spectroscopy.

Readers are strongly urged to consult these extremely interesting articles for a description of the elegant experiments involved. Other accounts of high-resolution laser spectroscopy of atoms are those by Happer (116C), Haroche (120C), and Barger, English, and West (9C). Clearly, these new methods open up new vistas for the accurate measurement of atomic spectra and fundamental constants and will be of both interest and use to analytical spectroscopists in the future.

Okino, Yamagishi, and Inaba (198C) and Phillips (207C) described the phenomenon termed radiation trapping and how it affects measured atomic fluorescence lifetimes. Radiation trapping occurs in a dense atomic cloud and results from multiple absorption and emission of the same photon energy before the photon can leave the medium. Clearly, the increased time a photon must spend in the atom cloud increases the probability of quenching of the excited-state energy and would affect a measured atomic fluorescence signal. Fortunately, radiation trapping is not expected to occur in flames, but might be of concern in electro-thermal atomizers, where rather dense clouds of atoms are produced. An important factor currently limiting the application of tunable lasers to analytical atomic spectroscopy is the difficulty of generating tunable ultraviolet radiation. Non-linear optical mixing and frequency multiplication in atomic vapors offers one solution to this problem and has been discussed by Wynne and Sorokin (251C, 299C), Royt, Lee, and Faust (230C), Bjorklund, Bjorkholm, and Freeman (22C), and Tanno, Adachi, Yokoto, and Inaba (266C). Excited-state absorption spectra of barium were obtained using a tunable laser by Rubbmark, Borgstroem, and Bockasten (231C).

~~Optics, Spectral Sorting Devices and Nondispersive Detection.~~ Goldstein and Walters (100C, 101C) discussed comprehensively the imaging of laboratory spectroscopic sources (flames, plasmas, etc.) onto monochromators. Any spectroscopist concerned with accurate spatial resolution within a source or optimal utilization of his spectrometric system should consult these articles. Coleman and Walters (54C) devised a simple mounting for use with a flexible optical bench system suitable for atomic spectrometry; La Croix and Wong (192C) described a simple collimating lens system for use in electrothermal atomic absorption spectroscopy.

Nagulin, Smolyak, Afanas'ev, and Gimushin (194C) devised a clever parallelogram mirror arrangement to enable the spiral scan of a flame and measured the flame radiation with a specially-designed trichromator. Kreye (166C) showed that a Fabry-Perot interferometer could be coupled with a conventional monochromator to enhance signal-to-noise ratios from both line and continuum sources. The use of fiber optics in a spectrometer was explored by Walrafen (289C), while Herkt and Müller (130C) described an easy technique for adjusting plane grating spectrometers. Shipp, Biggins, and Wade (240C) employed an electronically tunable acousto-optic filter to rapidly scan the entire visible wavelength region with a bandwidth of 2-6 Å. Such a filter, which is based on the acoustic production of a compression grating in a transmitting solid, appears to offer considerable promise for rapid scanning spectroscopy in the future.

Resonance monochromators have long seemed attractive because of their simplicity and ability to provide extremely accurate, narrow-band detection of atomic spectral lines. However, early resonance monochromators were limited in their convenience and in the range of elements they could

detect. Walsh (290C) has shown that a separated flame can be employed as a resonance detector and provides not only high detection efficiency but convenience of elemental selection as well. Van Loon and Radziuk (281C) explored this system further using a N_2 -sheathed air/ C_2H_2 flame as a resonance monochromator for the determination of several elements atomized in a graphite furnace. Unfortunately, detection limits were ten-fold worse than obtained with a conventional monochromator; noise in the detector flame was blamed. Dawson, Grassam, and Ellis (63C) designed a special electrothermal atomizer to provide a continuous supply of atomic vapor for use as a resonance monochromator. Again, rather large instabilities were observed and were ascribed to flicker in the vapor generator. Butler, Kroeger, and West (36C) found a glow discharge source more stable; however, it is apparent that the device would be far less convenient or flexible than a flame.

Dorofeev, Razyapov, and Chupakhin (69C) characterized the noise sources in a nondispersive atomic absorption photometer and found both additive and multiplicative noise sources present. Nondispersive atomic absorption and atomic fluorescence spectrometers were designed and applied by Chupakhin, Razyapov, Makarova, and Dorofeev (49C), Caupeil, Hendrikse, and Bongers (40C), Kuga and Tsujii (168C), and Stakheev and Stakheeva (253C).

Photodetectors and Detector Arrays. Hamm and Zeeman (111C) developed an inexpensive digitizer for photomultiplier currents which might find use in atomic spectrometry. Although most photomultipliers employed in atomic spectrochemical analysis do not require cooling, end-on photomultipliers or those having enhanced red response would benefit from the simple

cooled housing designed by Hoyt and Ingle (134C). Rayside, McLendon, and Fletcher (222C) have increased the linear range accessible by a photomultiplier tube by a factor of 10^6 through use of a servo-controlled shutter. The shutter senses the incoming light level and automatically opens or stops down to control the light incident on the detector. Such a device might find greater use with detectors such as the photodiode arrays discussed below, where dynamic range is a greater problem than in photomultipliers. A gain-control circuit for photomultiplier tubes is also able to control dynamic range and was described by Seda and Sabol (236C). Adams, Kirkbright, and Taylor (1C) demonstrated that a photoionization detector could be employed to advantage in nondispersive atomic spectrometry in the vacuum ultraviolet region. Techniques aimed at reducing the labor and inconsistencies involved in photographic detection were published by Blevins and O'Neill (23C) and Sambueva, Sverchinskaya, and Shipitsyn (234C).

A high level of activity continues in the development and exploitation of photodiode arrays and television-type readout systems. However, it now appears that such detectors are of limited general utility in atomic spectrometry and, with few exceptions, will not enjoy widespread use as multi-element detectors. This view is supported by several publications of Winefordner and his group. In a general evaluation of imaging detectors (photodiode arrays, vidicons, etc.), Cooney, Boutilier, and Winefordner (58C) concluded that silicon vidicon tubes are not analytically useful in atomic fluorescence spectrometry, whereas image dissector tubes and secondary electron conduction (SEC) tubes show promise, especially when coupled with Echelle cross-dispersion spectrometers. (Echelle spectrometers

are discussed in more detail in a following section entitled "Systems for Multi-element Analysis".) Moreover, the number of spectral lines which must be measured and the degree of flexibility required in choosing them governs whether the SEC/Echelle, image dissector/Echelle, a direct reading spectrometer, or wavelength-scanning technique will be superior. Chester, Haraguchi, Knapp, Messman, and Winefordner (46C) also showed experimentally and theoretically that a silicon-intensifier target (SIT) vidicon tube is of limited utility in atomic emission or atomic fluorescence spectrometry. Detection limits obtained with such a device are much worse than those generated with photomultiplier tubes, especially for ultraviolet spectral lines. The authors flatly state that the SIT tube, the image vidicon, solid state photodiode arrays, and probably the intensified SIT tube are not recommended for use in analytical atomic emission or fluorescence spectrometry. This conclusion is supported by the study of Yates and Kuwana (302C), who found extremely low sensitivity with their solid-state linear photodiode array detector.

Despite their limitations in signal-to-noise ratio, sensitivity, and linear range, vidicon tubes and other television-type readout devices offer several convenience features which can be exploited. Felkel and Pardue (81C) combined a random-access vidicon tube with a specially designed Echelle spectrometer for multi-element atomic absorption determinations. The two-dimensional format of the Echelle display, coupled with the large number of resolution elements (pixels) of the vidicon provides a broad wavelength coverage (2250-8000 Å) at adequate resolution (ca. 1 Å). Random addressing of the vidicon face should enable any element or combination of elements to be examined; however, the hollow cathode lamp employed

with the described system limited elemental coverage. As the authors point out, the vidicon readout offers more promise in atomic absorption than in other areas of atomic spectrometry. A similar randomly addressed, computer-controlled vidicon device was constructed by Nieman and Enke (195C). Howell, Ganjei, and Morrison (132C) exploited the multichannel capability of an SIT tube in an internal standard analysis; Ganjei, Howell, Roth, and Morrison (98C) processed the computerized output of their vidicon detector to obtain least-squares polynomial curve-fitting, spectral stripping, background correction, and internal standard correction. Cook, Pardue, and Santini (56C) superimposed a sinusoidal modulation onto the horizontal electron-beam sweep within their vidicon system and employed phase-sensitive detection to perform derivative spectrometry in a manner similar to that used in repetitive wavelength scanning. The system was refined and characterized further in a later publication by Cook, Santini, and Pardue (57C) and in the thesis by Cook (55C). Significantly, Howell and Morrison (133C) compared silicon vidicon detectors with photomultiplier tubes and claimed that the former detector is suitable for the atomic fluorescence or emission determination of elements whose resonance lines lie above 380 nm.

Most of the work performed with linear photodiode array detectors has been by Horlick and many of the more important features of such devices are illustrated in his excellent review (131C). An innovative and highly useful application of linear arrays is the spatial profiling of spectral sources, as described by Franklin, Baber, and Koirttyohann (90C). In this method, the linear array is positioned vertically in place of the exit slit in a conventional stigmatic monochromator. Each of the diodes in the array then indicates the intensity of a small segment of any

spectral source imaged onto the entrance slit. Readout is rapid and signal averaging is convenient, enabling high spatial resolution to be obtained at any chosen wavelength. Edmonds and Horlick (74C) demonstrated the utility of the technique in characterizing an inductively coupled plasma.

A convenient feature of intensified SIT tubes is their ability to be rapidly gated, thereby enabling transient phenomena to be observed or time-resolved spectra to be obtained. This feature was exploited by Weber (293C) and by Schmidt, Gordon, and Mulac (235C) and instrumentation for the method was described by Simpson and Talmi (241C) and by Ostertag (203C). An interesting application of vidicon tubes was described by de Haseth, Woodward, and Isenhour (122C). Their computer-interfaced TV camera digitized infrared spectra which were imaged on its face. Clearly, such a device would be extremely useful in many areas of spectroscopy and would overcome many of the disadvantages of vidicon tubes which were cited earlier.

Microchannel plates had been heralded as one possible solution to the low sensitivity which plagues solid-state photodiode arrays and TV detectors. Basically, microchannel plates are merely closely-packed arrays of electron multiplier tubes and should be suitable for electron multiplication prior to detection by a solid-state photodiode array. Unfortunately, it is difficult to fabricate such a system with gains greater than 10^4 because of destructive ion feedback. This problem might be overcome if channels can be curved, such as described by Timothy and Bybee (271C) and characterized by Boutot, Delmotte, Milhe, and Sipp (29C). Other improvements in microchannel plate systems were reported by Timothy (270C),

Timothy and Bybee (271C), and Wiza, Henkel, and Roy (296C). A far ultraviolet spectrograph incorporating a microchannel plate detector was constructed by Lawrence and Stone (175C).

Systems for Multi-Element Analysis. The development of new methods for multi-element atomic spectrometry continues to attract more and more workers. The many alternative approaches can be broken into several categories according to the technique they employ (emission, absorption, or fluorescence) and the manner by which spectral selection is accomplished. Winefordner, Avni, Chester, Fitzgerald, Hart, Johnson, and Plankey (295C) categorized readout methods as multiplex (Fourier transform and Hadamard transform spectroscopy), sequential linear scan (SLS), sequential slew scan (SSS), or multichannel (direct-reader) approaches. Signal-to-noise calculations showed that the multichannel approach is generally best and the SSS system falls closely behind, especially when UV-visible spectra are simple. Multiplex techniques will ordinarily not be useful in the UV-visible region when spectra are complex or where background shot and/or fluctuation noise are dominant. This latter point is amplified by Chester, Fitzgerald, and Winefordner (45C); for weak spectral lines in atomic absorption, emission, or fluorescence, a multiplex disadvantage will commonly exist and rule out Hadamard transform or Fourier transform spectroscopy in most practical applications. Even the throughput (Jacquinot) advantage, frequently cited as a reason for adopting a multiplex technique, is questioned by Chester and Winefordner (44C). Ordinarily, comparisons between dispersive and multiplex spectrometers assume equal resolving power, whereas such resolving power is not often required, particularly if modulated

line sources are employed which can be readily distinguished from adjacent spectral background. For example, a modulated spectral line from a hollow cathode lamp can be readily distinguished from adjacent background through frequency-selective detection, permitting the use of a far wider entrance slit and greater throughput in a dispersive spectrometer. Hirschfeld (126C) also considered the multiplex (Fellgett) advantage in UV-visible multiplex spectroscopy and concluded that either an advantage or disadvantage might arise depending on the complexity of the spectrum being observed and whether emission or absorption is employed. Hirschfeld (127C) also discussed the implications of fluctuation noise in multiplex spectroscopy.

Theoretical arguments notwithstanding, Keir, Dawson, and Ellis (152C) applied Hadamard transform spectrometry to the multi-element determination of Mg and Pb. Not unexpectedly, detection limits were poorer than obtained with a conventional AA system. The authors present an excellent introductory explanation of the Hadamard transform procedure. Yuen and Horlick (303C) modified their interferometer employed earlier in Fourier transform atomic spectrometry to permit phase correction of the transformed spectra and, once more, show the utility of aliasing. Pruiksma, Ziemer, and Yeung (218C) employed a Fabry-Perot interferometer and an oxy-hydrogen flame for multi-element detection, but obtained rather unimpressive signal-to-noise ratios.

Continuum-source atomic absorption spectrometry offers one alternative method for multi-element analysis. One of the most attractive new approaches to continuum-source AA employs an Echelle spectrometer and any one of a variety of readout systems. Keliher and Wohlers (154C) provided an overview of these systems and (153C) extended their earlier studies on them

to ultraviolet wavelengths. For the ultraviolet work, it was necessary to employ an Echelle spectrometer with far greater throughput and a more efficient spectral continuum source. Zander, O'Haver, and Keliher (304C, 305C) combined wavelength modulation with a high-resolution Echelle spectrometer to obtain increased working curve linearity, convenient correction for non-specific background absorption, and almost complete freedom from spectral interference from non-analyte lines. Although detection limits and sensitivities are somewhat worse than obtainable with conventional line-source atomic absorption, the multi-element capability of the device far outweighs these limitations. O'Haver, Harnly, and Zander (197C) reduced stray light in their wavelength-modulated Echelle spectrometer to obtain even better "characteristic concentrations" (previously termed "sensitivities"). Harnly and O'Haver (119C) utilized a similar device for background correction in graphite furnace atomic absorption. An entirely new approach to continuum-source atomic absorption was characterized by Cochran and Hieftje (51C). In the new approach, continuum radiation is passed through a flame in which the atom concentration is periodically raised and lowered. Radiation transmitted by the flame then is modulated, but only at wavelengths corresponding to atomic absorption lines. Frequency-selective amplification at the modulation frequency then makes the combination of continuum source and modulated flame appear similar to a modulated hollow cathode lamp containing the combination of elements which are modulated in the flame. Incorporation of the "combination source" into a conventional atomic absorption spectrometer then enables multi-element detection, using any desired atomization device. Characteristic concentrations (sensitivities) and working curve linearity

approach those obtainable with a hollow cathode lamp and were far better than those available from conventional continuum-source atomic absorption. More detail can be found in the thesis by Cochran (50C). Other aspects of continuum-source atomic absorption were explored by Slavnyi, Astaf'ev, Mogilevskii, Subochev, and Fabelinskii (246C), and Furuta, Haraguchi, and Fuwa (96C).

Danielsson and Lindblom (61C) coupled a randomly-addressed, micro-computer-controlled image dissector tube with a coma-corrected, low astigmatism Echelle spectrometer to yield a system which should be quite useful for absorption, emission, or fluorescence spectrometry. Of course, the image dissector tube is essentially a scanned device and has no storage capability, making it fundamentally somewhat inferior to a multi-channel system. Johansson and Nilsson (142C) devised a special grating with five independent vertical sections, each with a groove spacing appropriate for diffracting a different spectral line onto the same exit slit. Consequently, five separate lines would appear at the exit slit, but vertically displaced from each other. A fiber optic bundle separated the vertical sections and directed the radiation to a single photomultiplier tube which viewed each of the segments sequentially by means of a chopper wheel. Chester and Winefordner (42C) modulated two spectral lamps at different frequencies and detected the induced fluorescence from two elements with a solar-blind photomultiplier tube. Although a Cl_2 filter was employed to reduce flame background, a multiplex disadvantage was observed, limiting the attractiveness of the technique for practical analyses. Other instrumental components useful for multi-element atomic spectrometry were described by Boumans, van Gool, and Jansen (27C),

Lundberg and Johansson (177C), and Alder, Alger, Samuel, and West (2C).

Because it is necessary to select compromise conditions for the atomization of different elements in an analytical flame, Brost, Malloy, and Busch (32C) devised a response parameter which permits mathematically simple selection of such conditions. Boumans (26C) compared a number of sources for multi-element analysis, including high-temperature flames, dc, microwave, and radio-frequency plasmas. Browner (34C) compared different primary sources for use in multi-element atomic fluorescence spectrometry; the thesis by Chuang (48C) examines in detail the utility of the eimac source in such an application. Fiorino, Jones, and Capar (84C) described a simple sequential technique for multi-element atomic absorption.

Automation and Optimization of Flame Spectrometers. The brief review on recent applications of digital computers in analytical chemistry by Perrin (205C) contained a short section on automation in atomic spectrometry. However, the theses by Woodruff (297C), Hunter (136C), and Routh (229C) dealt in detail with the automation and optimization of flame spectrometers and with the construction of devices useful in such endeavors. Spillman and Malmstadt (252C) described a new computer-controlled programmable monochromator system useful for atomic spectrometry which incorporates a quartz refractor plate for on-line wavelength centering and correction for misalignment. The inexpensive digitizer for photomultiplier currents designed by Hamm and Zeeman (111C) and the new kind of analog-to-digital converter of Frazer, Hieftje, Layman, and Sinnamon (91C) should also find application in automated flame spectrometry. Optimization of flame spectrometric procedures will be rendered more efficient by the new simplex

routine of Routh, Swartz, and Denton (228C). The new algorithm requires fewer simplices, data points, and less time. Moreover, the routine is relatively noise-immune and adheres less frequently to false ridges than would a conventional simplex.

One of the most time-consuming aspects of atomic spectrometric analyses is sample preparation and surprisingly little attention has been paid to the automation of this phase of laboratory work. The automated solution handling system described by Renoe, O'Keefe, and Malmstadt (227C) should help substantially in automation of this phase. The new system employs an electronic balance which feeds back via a computer network to a reagent dispensing system. Extremely accurate volumes (or weights) of desired reagents can then be added in a desired sequence to fully automate sample preparation. A simple automated sample preparation device based on a commercial wet-ashing apparatus was constructed by Frank (89C). Similarly, Falinower (79C) employed a pneumatic logic network to automate the atomic absorption analysis of cements, sands, and limestones.

Several workers have automated hydride generation procedures for the flameless determination of Se, As, and Pb. Included in this group are Fishman and Spencer (85C), Pierce, Lamoreaux, Brown, and Fraser (211C), Pierce and Brown (210C), and Vijan and Wood (283C, 284C). Poldoski (212C) adapted a turnkey chromatographic data system to the automation of furnace atomic absorption.

Signal Processing in Atomic Spectrometry. The controversy continues whether peak height or peak area serves as a better measure of atom concentration in electrothermal atomization atomic absorption spectrometry.

Issaq and Young (141C) claim that peak height measurements provide greater working curve slope than does peak area, but their displayed working curves are calibrated in non-absorbance units, making the claim difficult to verify. In contrast, Cantle (37C) has shown that integration of transient signals can improve accuracy. To us, precision and accuracy (i.e., signal-to-noise ratio) is more important in an analytical measurement than is working curve slope. Moreover, integration of transient peaks observed in electrothermal or flame-based atomic absorption aids in overcoming changes in volatilization rate caused by sample matrix. Consequently, it would seem that peak integration would in most cases be preferable to peak height measurement. It is worth noting that many so-called peak height measurements are actually representative of peak areas because of the relatively slow response of the recording system which is used, compared to the true length of the transient atom pulse. Piepmeier (208C) has shown that tailing peaks or those having extensive "wings" can be integrated with greatest precision if the wings or tail of the peak are not included in the integral. Inclusion of these features merely adds noise to the integrated signal and does not materially increase the signal value itself. Bertram, Taphorn, Robbins, Younginger, and Caruso (19C) designed an electronic integrator intended for use in non-flame atomic absorption spectrometry.

Piepmeier and de Galan (209C) derived a theoretical expression which accounts for changes in source and absorption line spectral profiles which occur when either source or atom cell is pulsed. Different kinds of signal processing systems were assumed, including lock-in amplification,

boxcar integration, and simple low-pass filtering. Significantly, apparent deviations from Beer's law can occur even for a monochromatic source if the sample absorption line profile is time-dependent. Mitchell, Mills, and Garden (191C) proposed a new multiple-curve procedure for improving precision which would be applicable to all flame spectrometric methods. Individuals who employ photon counting in their atomic measurements would benefit from the publication of Hayes and Schoeller (123C), which quantitatively examines the influence on precision of deadtime uncertainty and count rate. Similarly, the versatile Fourier-domain digital filter devised by Betty and Horlick (20C) would be useful to those who digitize their data or employ computer-controlled instrumentation. Haraguchi, Furuta, Yoshimura, and Fuwa (118C) employed an analog magnetic tape recording system followed by signal processing devices to implement baseline correction, background correction, etc., and thereby improve their results.

Zeeman Modulation and Other Background-Correction Methods. The most innovative and potentially useful method for background correction to be developed recently is that involving the Zeeman effect. In Zeeman modulation, a magnetic field is applied to either source or generated atoms to split the Zeeman components of each spectral line. Because these components are polarized, it becomes possible to isolate them using stationary or rotating optical polarizers. This "Zeeman modulation" can then be employed for high-precision background correction. Further details on this method can be found in the original articles by Koizumi and Yasuda (159C, 160C) and in the excellent overview by Brown (33C). Koizumi and Yasuda (161C) also explored the application of their new technique to the

determination of Pb, Cd, and Zn and found it possible to correct for background absorption up to an absorbance of 1.5. Dawson, Grassam, Ellis, and Kier (62C) explored background correction in electrothermal atomic absorption using the Zeeman effect in the atomized sample while Veinot and Stephens (282C) showed how the Zeeman effect could be employed to extend calibration curves somewhat. Stephens (256C) also applied the Zeeman effect to a capacitively-coupled radio-frequency plasma.

Repetitive optical scanning (wavelength modulation) is finding more and more application as a technique for background correction in flame emission, atomic absorption, and atomic fluorescence spectrometry. The thesis by Epstein (76C) discusses the application of wavelength modulation devices to emission spectrometry in detail, while that of Sydor (261C) compares wavelength modulation to several other methods for background correction. Koirtzmann, Glass, Yates, Hinderberger, and Lichte (158C) considered the effect of different modulation waveforms on the degree and fidelity of background correction which could be obtained by wavelength scanning using oscillating refractor plates. O'Haver, Epstein, and Zander (196C) also considered the effect of waveform and amplitude of modulation, the shape of the modulated spectral line, and the type of signal processing employed on repetitive scanning spectrometry. It was found that line shape is relatively unimportant, but square-wave modulation produces a signal-to-noise ratio which is twice as great as that obtained with sine-wave modulation, if the spectrometric measurement is limited by background-carried shot noise. Fitzgerald, Chester, and Winefordner (86C) and Chester and Winefordner (43C) described a new kind of wavelength modulation spectrometer which incorporates a diffraction

grating in one arm of a repetitively scanned Michelson interferometer. The signal-to-noise characteristics of the device were evaluated and its application to atomic spectrometry explored. Although signal-to-noise depends strongly on the nature of the observed spectral background, S/N is ordinarily lower than can be obtained with a conventional dispersive spectrometer, limiting the attractiveness of the new device for most practical measurements. Visser, Hamm, and Zeeman (285C) converted a conventional spectrometer to a wavelength-modulated device merely by opening up the entrance and exit slits, lengthening the spectrometer's focal distance, and adding two new slits, one of which is repetitively scanned. Sydor and Hieftje (262C) employed an oscillating interference filter to scan repetitively a fixed wavelength region and demonstrated the device's practical utility in background-corrected flame emission spectrometry. A rotating interference filter was also employed in the modulation photometer of Lyakhov and Managdze (179C). The dynamic background correcting system described by Skogerboe, La Mothe, Bastiaans, Freeland, and Coleman (243C) employed a refractor plate similar to those used in wavelength modulation, but repetitively shifted the plate into and out of the radiation path behind the entrance slit of their spectrometer. As a result, the slit image was moved back and forth in a square-wave pattern, enabling successive measurements of the desired spectral line and the background adjacent to that line. Because the detector can then view the desired radiation for a longer period of time, higher signal-to-noise ratios are possible. A new kind of quartz plate wavelength modulator, designed by Katskov, Kruglikova, L'vov, Orlov, and Polzik (151C) consists of a quartz disc, mounted at an angle on a motor shaft, so it rotates smoothly but

at an angle to the plane of rotation. As a consequence, the slit image nutates sinusoidally about the exit slit to produce wavelength modulation. The stepped refractor plate of Visser, Hamm, and Zeeman (286C) enables background on both sides of a spectral line to be observed at once. Epstein, Rains, and O'Haver (78C) applied wavelength modulation to carbon furnace atomic emission spectrometry and found that detection limits could be improved up to several orders of magnitude. Slavnyi, Subochev, and Mogilevskii (245C) compared wavelength modulation with dual-channel background correction and found the latter technique to be better. Doolan and Smythe (68C) and Wehrly, Williams, Jameson, and Kolb (294C) also studied dual-channel background correction techniques. Sydor, Sinnamon, and Hieftje (263C) corrected for background emission on both sides of a spectral line with the aid of a special secondary slit. A portion of the measured radiation was diverted from the primary monochromator entrance slit to a second, wider slit which was bisected by a fine wire blocking the desired elemental emission line. The secondary slit then transmitted only background radiation and enabled more accurate background correction of the primary signal.

Höhn and Jackwerth (129C) showed that the commonly used deuterium lamp scheme for background correction might yield either erroneously high or low results if the background being detected is highly structured. For example, background consisting of rotational or vibrational absorption lines of molecular species can generate positive or negative errors depending upon the relative positions of a particular band and the spectral line of interest. Hendrikx-Jongerius and de Galan (125C) evaluated other errors in the deuterium background correction method, including optical

path differences between hollow cathode lamp radiation and that from the deuterium source and those arising from excessively high broadband attenuation. In electrothermal atomization methods, where background correction is especially important, these potential errors can be minimized through judicious use of temperature programming to separate volatilization of sample matrix and the analyte of interest. Epstein and Rains (77C) extended background correction farther into the visible range through use of a xenon-mercury arc lamp in place of the conventional deuterium or hydrogen source.

Accurate instrumental subtraction of flame background can be accomplished by directly monitoring the background in a "reference" flame and subtracting it from the signal produced by an analytical flame. This dual-flame approach was employed by Haraguchi, Toda, Hirabayashi, and Fuwa (117C) in an absorption mode and by Urbain and Desquenness (280C) in emission. An extremely clever new method for background correction was devised by Araki, Uchida, and Minami (5C). Time-resolved studies of the radiation emitted by a pulsed hollow cathode lamp indicates that fill-gas lines increase in intensity more rapidly than do atomic lines, although atomic lines dominate later during the pulse. If a fill-gas line lies outside the absorption band of the desired elemental line but within the bandpass of the spectrometer being employed, time-gated detection can resolve the two sources of radiation and thereby enable background correction. Arsenault and Marmet (6C) compared a number of mathematical techniques for removal of background from digitized spectra, including high-pass filtering and differentiation. Both methods were capable of accurate background subtraction, but produced distortion and loss of signal-to-noise in the resulting narrow lines.

Other Instrumental Innovations and Evaluations. Surskii and Avdeenko (260C) described a simple arrangement for the automated calibration of a graphite-furnace atomic absorption spectrophotometer. In the method, a second graphite furnace is used to repetitively vary the atom concentration in the absorbing light beam by a known amount. The amount of absorption produced by this second vapor cell can then be related to the slope of a calibration curve, from which the concentration of the sample present in the first graphite furnace can be determined. Panichev, Prudnikov, Tatti, and Turkin (204C) employed a flame photometer coupled with a pulse height analyzer to determine quantitatively the composition of aerosol particles blown into the flame. Tomson, Barone, and Nancollas (274C) analyzed both Ca and phosphate with the same Ca hollow cathode lamp. While Ca could be determined through its resonance line at 422.7 nm, the same hollow cathode line could be employed for the determination of phosphate through absorption of the phosphovanadomolybdate yellow complex at 420 nm. It has occasionally been suggested that atomic resonance lines could be observed in solution, following reduction of metallic ions. This effect was studied by Umezawa, Fujiwara, Fujiwara, and Fuwa (279C), who concluded that the "atomic absorption" was probably due to hydrated atoms rather than the free species. Fragale and Bruno (88C) described a simple flame emission device for teaching laboratories which incorporates a Pt wire atomizer and a glass filter.

Background interferences caused by molecular fluorescence were observed by Fowler and Winefordner (87C). In an argon-separated air-acetylene flame, molecular fluorescence due to PO, NH, CN, and OH was observed. Significantly, PO was one of the major contributors to molecular fluorescence

and could be eliminated simply by employing a higher grade of acetylene. PO bands arise primarily from the oxidation of phosphine, which is a common contaminant in the acetylene obtained from many manufacturers. The presence of phosphine in acetylene can be discerned readily by the milky appearance of an air-acetylene flame. Scatter and molecular fluorescence interferences in atomic fluorescence spectrometry can be overcome through a correction technique devised by Haarsma, Vlogtman, and Agterdenbos (110C). In the method, the temperature of an electrodeless discharge lamp source is varied and the combined scatter/fluorescence signal observed. Because the atomic spectral profile of the lamp changes markedly with temperature, a greater fraction of the induced scattering/fluorescence is due to background at higher lamp temperatures. Observation of the relationship between measured signal and lamp temperature then enables correction for broad-band features.

Electrothermal and Cold Vapor Atom Formation Devices

The use of electrothermal atomization devices has dramatically increased since the last review. This section of the review includes articles dealing primarily with "non flame" techniques including carbon filaments and furnaces, metal filament atomizers, cold vapor devices, and hydride evolution techniques. Admittedly hydride evolution procedures often utilize diffusion flames but their chemical similarity to Hg evolution techniques seem to warrant inclusion in this section. Techniques such as MECA, candoluminescence and chemiluminescence are reviewed in section F.

Reviews and general discussions. Sturgeon (74D) has reviewed carbon furnace atomization devices and presents a detailed discussion of problems associated with commercially available devices (spatial and temporal non-isothermality, peak height vs area measurements atom diffusion into non-pyrolytic graphite, etc.).

Further problems associated with transient atomic vapor clouds and cw or pulsed sources and detection systems are discussed by Piepmeier and de Galan (60D). Several instances where Beer's Law is not obeyed are given. Nemets, et. al. (51D) discuss the physical dimensions of the atomic vapor cloud above an open carbon cup atomizer. Sturgeon and Chakrabarti (77D) discuss the excitation temperature of the atomic vapor in a carbon tube furnace and describe a 2 line method for measuring temperatures. The same authors (78D) found that increasing the pressure of the atomizer (to 13 atm) may confine the atomic vapor to the furnace for a longer time but reduces both peak heights and areas (Lorentz shift of the absorption line). An increased linear working range was achieved at the higher pressures. A two line method for temperature measurements to 3200°C is described by Tsujino et. al. (86D). The melting point of Au was used for standardization. Temperature characteristics such as time/temperature relationships as a function of dry, ash and atomize voltages and applied wave-forms (step, ramp, etc.) were presented by Hoshino and Utsunomiya (32D).

The precision and accuracy of graphite atomizer analyses are discussed by Welz (95D) and Garnys and Smythe (22D). Woodriff, Amend, and Bath (96D) discuss background correction, multielement analyses, and matrix effects in the constant temperature Woodriff furnace. Finally, in a review of the interferences, contamination problems, sample handling problems etc., Fuller (18D) asks "A routine or specialist analytical technique?" Good question.

Atom formation and loss. The continuing problems of matrix interferences in electrothermal atomizers has led to several investigations of the rates and mechanisms of atom formation in carbon furnaces. Torsi and Tessari (85D) found the release of Pb atoms in a H_2 environment to follow a previously developed theory which assumes a monolayer or less coverage at the carbon surface and a first order kinetic atom release process. Fuller (21D, 19D) has used a model which assumes a first order reduction of the metal oxide at the carbon surface to examine the rate of atom formation and loss and atomization efficiency and discusses how atomization parameters might be adjusted to alleviate matrix problems. Atom loss from a constant temperature furnace (97D) was found to occur via two different mechanisms simple diffusion (Ag, Cd, Zn) or diffusion complicated by carbide formation at high temperatures (Mn, K, Cu). Frech and Cedergren have applied high temperature equilibrium calculations to explain the mechanism of a chloride interference on lead. For Pb analysis in steel samples (14D, 15D) addition of H_2 to the sheath gas was found to aid in the removal of Cl (by forming HCl rather than $PbCl$, $PbCl_2$, or $FeCl_2$). For Pb analyses in NaCl matrices (16D) both a high non-specific absorption and a 20% loss in sensitivity over distilled water standards were observed. Addition of HNO_3 reduced the non-specific absorption (evolution of HCl and $NaNO_3$) but did not improve the sensitivity. Co-volatilization of Pb was the postulated cause. Ottaway (54D) maintains that although a reducing carbon surface can promote metal formation by reduction of the metal oxide, these reducing conditions do not exist except at the atomizer surface. Therefore, salts which would volatilize before the reduction step was thermodynamically feasible would be atomized only by a thermal decomposition process. Matrix salts such as chlorides which are volatile and do not decompose to an oxide would thus interfere more than oxanions which can decompose to the oxide. Yasuda and Kakiyama (101D, 102D) measured molecular spectra above a carbon tube atomizer at temperatures from $150^\circ C$ to $2600^\circ C$ and found SO_2 and NO_2 from sulfate and nitrate solutions as well as undissociated metal halide spectra ($CrCl_2$, $CoCl_2$, MnF_2 , Cu_3Cl_3 , $CoBr_2$, etc.) from halide matrices. Pritchard and Reeves (63D) found alkali halide charge transfer spectra to comprise most non-atomic absorption with 3 different carbon atomizers (rod, cup, and tube). Only small (non-Rayleigh) scattering signals were observed.

Sturgeon and Chakrabarti (76D) have found that the major mechanisms of atom loss for a Perkin Elmer HGA 2100 carbon furnace are condensation on the cooler

extremities (ca 60%), loss through the sample injection port (20%) and loss through the graphite walls. Using a combined kinetic and thermodynamic approach Sturgeon, Chakrabarti and Langford (79D) have proposed mechanisms of atom formation for the same atomizer. The theory assumes that an analyte surface - gas phase equilibrium exists, that atom production is characterized by a unimolecular rate constant and that at least for lower temperatures the furnace atmosphere and walls are at the same temperature. For measurements taken for the first few hundred milliseconds of atom production, atom formation was found to occur either by thermal decomposition of the oxide or chloride or by carbon reduction of the metal oxide. For a surprising number of elements, dimeric species appear to exist. Corrections of equations and graphs (80D) and in the proposed atom formation mechanism for Al (no mechanism which explains the data is given) (81D) are brought to the reader's attention.

Hiroq (30D) has measured the physical size of copper and uranium deposits on a carbon filament by monitoring the ion current after bombarding the deposit with an O ion beam. He has also studied the size of the atomic vapor cloud above a carbon filament as a function of atomization temperature and carrier gas flow (29D).

It is evident that although a great deal of effort has been expended in elucidating the exact mechanism(s) of atom formation universal agreement has not been reached. Results seem to show that the mechanism of atom formation is different for different elements (due to differing oxide stabilities, propensities to volatilize, be reduced by carbon, tantalum, dimerize, etc., different matrices (chlorides and oxides/oxyanion moieties showing marked differences) and different atomizers (rates of heating, atomizer containment volume, and atom loss mechanisms all being atomizer dependent). The complexity of this problem is clearly manifested in the number of interferences observed for various matrices and in the number of procedures for minimizing or eliminating matrix effects.

Interferences in electrothermal atomizers. Czabik and Matousek (11D) measured atomization temperatures in the presence of various anions. Only phosphate was found to change the appearance temperature and only for elements normally atomizing at temperatures lower than Sn. They conclude this supports two mechanisms of atom formation reaction with carbon at low temperatures and thermal decomposition at higher temperatures. Numerous cations were found to interfere with determination of Fe, Co and Ni (49D). Although some degree of interference was noted for all cations, those having appearance temperatures near

that of the analyte were most severe.

Strong acids and oxidants were found to suppress the atomic absorption signals of Fe, Co, Ni, Ag, and Cd (88D) and reactivity of the graphite atomizer was offered as the major cause of the suppression. Fuller (20D, 17D) has reported that HNO_3 and H_2SO_4 have slight suppressive effects on Tl while HCl and HClO_4 cause severe signal reduction. Further, in the presence of NaCl which also interferes, H_2SO_4 reduces the effect of NaCl. Both positive and negative interferences were found for various chlorides, nitrates, phosphates and sulfates on the absorption signals for Cu and Mn (71D). Most negative interferences were affected by the ash time and temperature and were therefore postulated to be due at least in part to the occlusion of the analyte.

Walsh, et. al. (89D) found that as absorbances were lowered when both Na^+ and SO_4^{2-} were present in solution and that addition of Mg^{+2} reduced the effect. Henn (28D) found that Mo was useful in eliminating interferences in the determination of Pb, Cd, and Se in natural waters. Presumably either selenides or heteropolymolybdates were formed which minimized the natural matrix effects.

Vapor phase interferences were the postulated cause for the suppression of Li by CaCl_2 (37D). The CaCl_2 decomposes and LiCl then forms unless H_2SO_4 or H_3PO_4 are present which form HCl and CaSO_4 (PO_4) in the ash cycle. Ohta and Suzuki found that Mg signals are depressed in the presence of Cr (53D) and that Pb is depressed by I^- , NO_3^- , or carbamates (52D). Ashing at 750°C or more minimized the interferences caused by lead or copper salts on the absorption signal of Ag (26D). To minimize carbide formation in the determination of Ba in silicate rocks, Cioni, et. al. (9D) filled the atomizer with a slurry of TiO_2 and fired it. The TiC_2 formed prevented BaC from forming. The analysis of Se was made possible by the addition of ascorbic acid or Ni to the cup (36D). Se metal or NiSe are preferentially formed rather than the volatile SeO_2 . Ascorbic acid was found to yield both rhombic and tetragonal PbO when heated in a crucible with $\text{Pb}(\text{NO}_3)_2$. This was manifested in double peaks in the analyses of Pb in ascorbic acid solutions (48D). Warren, et. al. (90D, 64D) found that ascorbic acid in fact enhanced Cu and Ga signals and eliminated the interference of Ca Mg Sr and Ba on Pb. They postulate that finely divided carbon is formed in situ which enhances the $\text{MO} + \text{C} \rightarrow \text{CO} + \text{M}$ mechanism of atom formation. Thompson, et. al. (84D) found that H_2 ascorbic acid, oxalic acid, NH_4NO_3 and several dithio carbamates were ineffective in eliminating matrix interferences in river water analyses. The natural water

samples were high in Ca and Mg content. The authors found that interferences for Pb and Cd could be minimized by coating the carbon tube with La.

For a Ta metal atomizer, Ueda (87D) found that interferences were minimized when a low drying temperature was followed by as rapid a heating rate as possible.

Wegscheider et. al. utilized factorial experimental design to determine interference effects on Pb, Cd, and Zn. They found that F^- and the cross term F^-/PO_4^{-3} interfered with Zn determinations (93D) and that these interferences were strongly dependent on ash time and temperature and that all mineral acids except HF interfered with Pb determinations (94D). They also found that Co, Cr, Ni, Si, Hg and Zn interfered with Pb and (somewhat surprisingly) that an ash temperature of 900°C minimized the interferences. Anderson (4D) found a severe interference of SO_4^{-2} on Pb could be eliminated by the addition of La to the analytical solution.

Instrumentation. Cox (10D) describes the construction of a simple, useful transformer/triac based power supply for small carbon tube atomizers. The system provides feed back control of the heating via a photodiode network. Aspila and Clignett (5D) describe the use of a sequential relay timer for auto zeroing and controlling dry, ash, and atomize times. Stoeppler, et. al. (73D) developed an automated sample introduction system for a graphite furnace. Sample "carry-over" (memory effects) were shown to be minimal using ^{89}Sr for radio tracer experiments. Sperling (72D) modified a carbon furnace by using a quartz window on one end to gain better control of the gas flow and hence atom cloud in the furnace. Afanas'ev (2D) developed a simple power supply with control of time and temperature being reproducible within 2%. Characteristics of a graphite tube atomizer capable of operating in both an isothermal and pulsed heating mode were described by Grushko, et. al. (25D). An optical system for modifying a flame AA for non-flame work was described by La Croix and Wong (39D). The system performance was checked using NBS orchard leaves. Watne and Woodruff (91D) describe a simple device using a solar cell for constant temperature monitoring in a Woodruff furnace. Reproducibility problems at temperatures below 1000°C were due to poor spectral response and at temperatures above 2000°C problems were due to severe non-linearity and poor sensitivity. The advantages of pyrolytic coatings on graphite tube atomizers were discussed by Sturgeon and Chakrabarti (75D). The pyrolytically coated tubes had slightly lower heating rates but reduced atomization times since the sample did not diffuse into the pyrolytic coating. Increased sensitivities were observed for Mo and V but not for Cd, Zn, Cu, Al or Sn. A small carbon tube

furnace system with a vacuum monochromator, EDL source and inert gas purged optical path was used for the analysis of S in solution (1D). Although non-linearity was observed for absorbances <0.3 less than 1 ng of S was quantifiable.

Sample Introduction. Marinkovic and Woodriff (45D) examined the effects of the sample introduction crucible on temperatures in the Woodriff furnace. They found that optimal results were obtained for crucibles with low mass and large surface areas (to enhance radiative heat transfer). Gregoire and Chakrabarti (24D) found that a rectangular platform of pyrolytic graphite for sample introduction unto a graphite furnace afforded slight enhancements for Mo and V but significant decreases for Cu.

Milled chips of nickle-based alloys were weighed and directly inserted into a graphite furnace. Using alloy based standards Pb, Bi, Se, Te, Tl and Sn were determined with relative standard deviations from 7 to 25% (46D). Lord, et. al. (42D) analyzed freeze dried tissue samples (fresh water mussels) by direct injection of the solid into the graphite furnace. To facilitate weighing of the small samples, naphthalene was used as a diluent. Aqueous standards were adequate for most elements but not for Pb and Zn.

Several groups used an electrolytic preconcentration step to circumvent matrix problems and/or low concentrations. Deldime (12D) plated Hg onto a Pt wire using controlled potential coulometry. The Pt wire was then resistance heated to drive off the Hg. Using this procedure 10^{-10} M solutions could be analyzed with 4% relative standard deviation. Dogan and Haerdi (13D) used a micro column of Cu powder and sample volumes of 10 to 1000 ml. The reaction $\text{Cu} + \text{Hg}^{+2} \rightarrow \text{Cu}^{+2} + \text{Hg}$ provided efficient and rapid separation of the Hg. Lund, et. al. (43D) electro deposited Cd at -1V vs SCE for 5 minutes onto a Pt wire. The wire subsequently was resistance heated and the Cd absorption determined in a quartz windowed cell. The procedure effectively separated Cd from a wine matrix. Thomassen, et. al. (82D) used exhaustive electrolysis (15 hours) at -1.0V to deposit Zn, Cd, Pb and Cu onto a graphite rod which was ground and analyzed in a graphite furnace. Hoshino, et. al. (31D) used a W wire to preconcentrate traces for alkali salt matrices.

Cold vapor Hg evolution. Christmann and Ingle (7D) have investigated several methods to prevent or minimize losses of Hg to container walls. They found that HNO_3/Au (III) or $\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$ minimized the losses, gold being more reproducible. They also found that using a column of heated 1mm glass beads rather than a dessicant was a more reproducible procedure for elimination of

water mist in the absorption cell. The same authors (8D) used a standard (1ppm) Hg solution for the indirect determination of Sn (II). The size and shape of the peaks evolved were critically dependent on the Hg concentration and HNO_3 was found to interfere. Pb shot was added to all samples to insure that Sn was present as the divalent cation. Organic mercury compounds in soil sediments were determined by a rather complicated method (47D). The sediments were extracted into benzene, glutathione and NH_4^+ were added, and the Hg back extracted into H_2O (which had been stored ≥ 1 week to assure that it was Hg free). The Hg was then reduced using Cu^{+2} , NaOH, SnCl_2 , collected on gold and determined in a standard cold vapor cell.

Litman, et. al. (40D) recommend using Neutron activation analysis if possible due to losses in both wet ashing and freeze drying procedures. Adsorption onto glassware was minimized by washing the glassware with dichromate. Alternatively, a dry ash/combustion procedure was used by these authors and others (23D) with minimal loss of Hg. Koirtjohann and Khalil (38D) found that $>1\text{ppm}$ Ag, Au or Pt interfere with Hg evolution and that some component of a polypropylene syringe caused premature reduction and evolution of the Hg. They recommend that solutions contain a strong oxidant and excess Cl^- . Thomerson (83D) optimized an AF procedure for Hg by sheathing the outlet of the cell, restricting the lamp aperture to lower specular reflectance, and cooling the Hg source for stability. Skidmore (70D) found that diluting the evolved Hg vapor stream eliminated the need for dessicants to prevent fogging of the cell windows. Narasaki, et. al. (50D) found enhanced sensitivity would be obtained by performing the reduction in a stirred Sn (II) solution with collection of the evolved vapor for 2 min then rapid introduction into the absorption cell.

Simpson and Nickless (69D) used a dual cell system to improve throughput. They also recommend dichromate and HNO_3 as additives to the solutions to prevent adsorption. Littlejohn, et. al. (41D) found that complexation of the Hg with cysteine was effective in preventing adsorption and determined "inorganic" and "total" Hg in urine. Seeger (66D) digested lyophilized mushrooms in $\text{KMnO}_4/\text{HClO}_4$ for 1 hour in a polyethylene and found 7 to 20% loss of Hg.

Several procedures using NaBH_4 as the reductant have been reported with somewhat divergent results. Rooney (65D) determined Hg in paint, blood and foodstuffs using acidic borohydride (no Hg evolution occurred from basic solution). He found that Cu, Bi, Au, Pt, Pd, Rh and Ru interfered. A small interference from Ag was believed to be caused by Au in the Ag. Lyashenko and Stepanov (44D) used borohydride in $\text{pH} > 12.5$ solutions and found rapid evolution

and interference from Ag.

Hendzel and Jamieson (27D) developed an automated system for analysis of fish tissues. They used an Al block on a vibrating hot plate for the digestion. The digestion mixture was 1:4 $\text{HNO}_3/\text{H}_2\text{SO}_4$. Pearce et. al (59D) compared Teflon bowls, Kjeldahl flasks and glass test tubes for wet acid digestion of fish and found no significant differences. They also found no Hg loss occurred if the fish were cooked at 170°C for 30 minutes prior to digestion which is disappointing to at least the Bostonian author of this review.

Hydride evolution. Yamamoto, et. al. have reported several methods for analysis of As, Sb and Se using NaBH_4 and Zn as reductants. They found the acidic Zn reduction system to be more selective than borohydride (99D) particularly for As. Most interferences which occur when using borohydride may be eliminated by the addition of KI (98D). This procedure was shown to be sensitive and interference-free for the determination of As in natural waters (100D).

Ito, et. al. (35D) used a Zn/HCl system to determine Sb. The detection limit was 0.1 ng and HNO_3 was found to interfere. Siemer, et. al. (68D) used a borohydride reduction of As. Sample solutions were highly acidic (HCl) and contained KI to insure that As (III) was the sole As species. H_2 rather than Ar or N_2 was used to sweep the generated H_3As into a rich H_2/O_2 or H_2/air flame in a long path (12cm) quartz tube atomizer. In later experiments, Siemer and Koteel (67D) achieved higher sensitivities for As and for Se by freezing out the hydrides in a liquid N_2 cooled u tube for subsequent introduction into the quartz burner.

Pierce and Brown (61D) investigated the interference effects of an extensive array of anions and cations on As and Se hydride generation and flameless AA procedures. HNO_3 , Sn, Co, Cu and Ni were the strongest interferants. Broughton and Fuller (6D) also investigated the effects of traces of transition metals on Se, Te, Bi, As and Sb hydrides. They found that there were minimal effects using an electrically heated (850°C) tube atomizer. Pierce, et. al. (62D) describe an automated system using a proportioning pump and auto sampler. Excellent agreement with results from a manual system were obtained for both As and Se.

Carbon furnace emission. Hutton, et. al. (33D) determined Ba in CaCO_3 rocks by measuring the emission from a graphite furnace at 2700°C CaOH bands interfere and a background correction procedure (wavelength modulation) was used. Later experiments (56D) showed that addition of 60 ml/min H_2 to the Ar purge gas also eliminated the CaOH interference. Hutton, et. al. (34D) also

observed molecular spectra of CN, C₂, CaO, SrO and MgO in the furnace.

Volatile elements may diffuse from the furnace before emission occurs (57D). This problem is circumvented by using a graphite furnace with thin walls at the ends which heat more rapidly than the thick center where the sample is deposited. Ionization has been shown to occur in furnaces (55D) and ionization suppression can be achieved eg. addition of Cs to Ba. The degree of ionization is much less than in nitrous oxide acetylene flames and results in no appreciable change in signal. Ottaway and Shaw (58D) have found the emission signal to be almost exponentially dependent on temperature and used modified furnace tubes with thinner walls to achieve higher temperatures. Alder, et. al. (3D) determined the excitation temperature of Fe using a two line method and found an excitation temperature of 2450°K with a furnace wall temperature of 2420°K. They conclude the excitation mechanism is purely thermal and report detection limits from 5 to 150 pg for Al, Cr, and Mo.

Analytical Comparisons and Figures of Merit

Comparison between atomic spectrometric techniques and other methods of trace analysis continue to be made and generally predictable conclusions are drawn. Neutron activation seems slightly less prone to matrix interferences than atomic absorption while electrochemical procedures require more careful digestions and control of matrices. Cost per analysis discussions generally reverse the order of the preceding list.

Pierce, et. al. (27E) conducted an interlaboratory study on the determination of Cr in urine, bovine liver and wheat. The techniques employed were neutron activation - irradiation for 100 hr, distillation as chromyl chloride and precipitation as BaCrO_4 ; furnace AA which required $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion; and gas chromatography which required derivitization to the trifluoroacetylacetate. Wide inter-lab variations were observed for wheat and inter- and intra-lab variations for bovine liver.

Moauero, et. al. (26E) found that sensitivity for Mn, Cu and Ca was higher for NAA than AA for plant tissue while the reverse was true for Fe, K, and Zn. NAA was preferred since no digestion was required. Behne, et. al. (2E) compared NAA and AA for the determination of Cr in brewer's yeast. They found that direct injection of yeast into a graphite furnace or wet digestion yielded lower results than NAA. Only AA after digestion in a pressure bomb compared favorably with NAA. May and Presley (24E) analyzed crude oils for Fe and Ni. AA yielded results which were higher than NAA for Ni but lower for Fe. The same authors (23E) analyzed beach asphalt for V and found flameless AA to be less precise than NAA.

Several studies have compared xray with AA, AE, or both. Prager and Groves (28E) determined Pb in glassware by gravimetry, xray fluorescence and flame AA. The AA was more rapid and no significant difference in the methods was found which is somewhat suprizing considering the spectra overlap of Pb and K lines at the 261.4 nm line used. Kozlicka and Romanska (17E) determined Cu in ores by x-ray fluorescence, AA and titrimetry and found no significant difference at the 95% confidence level. Brenner, et. al. (8E) analyzed silicate rocks by AA, d.c. arc, and x-ray fluorescence. They conclude that observed differences in a few results are explicable by differences in sample preparation and the precision of the methods.

Signals, noise, precision, accuracy and detection limits. L'vov (21E) discusses various procedures for estimating and comparing detection limits in atomic absorption. Belyaev, et. al. (3E) compare sensitivity, precision and detection limits for graphite atomizer AA and AF. They find that AF has lower limits of detection and higher sensitivity but that the precision of AA is better at moderate and high concentrations. They recommend a dual channel instrument to record both signals simultaneously. Belyaev (4E) also used simultaneous, d.c. arc emission, flame AA, for improvement of the precision in rock analysis. Bower and Ingle (6E) demonstrated that the precision of flame AA of Cu is not limited by source flicker noise or signal shot noise or the typical amplifier readout system but rather by noise due to fluctuations in the transmission properties of the flame (at small absorbances) and fluctuations in analyte absorption properties at large absorbances. The same authors (7E) refined procedures for evaluating the precision of flame AA analyses and applied the evaluation methods to 9 elements. Again, at moderate absorbances, analyte absorption flicker limits precision.

Milham and Short (25E) found that a $\pm 2^\circ\text{C}/\text{day}$ temperature fluctuation caused as much as a 0.02 absorbance unit shift in a single beam AA. Components most affected were the photomultiplier, the amplifier, and the hollow cathode lamp. Höhn and Jackwerth (16E) discuss non compensatable background (spectral overlap, etc.) in AA and demonstrate the problem with the analyses of Au in InCl_3 . Hansen and Hall (10E) describe a general "cure all" (or most) technique for reducing ionization and interelement interferences. The method which is simply to use a 0.4% CsCl 2% HCl matrix for everything was tested for 14 elements in glass, minerals and metals with interferent-to-analyte ratios of 33:1. For this limited excess of interferent range the procedure worked well.

Betty and Horlick (5E) describe a simple digital filter based on a trapezoidal function which was utilized for smoothing, differentiation, resolution enhancement and deconvolution of spectral signals. Hareland (11E) discusses analyses and characterization of noise in flame spectroscopy.

Hirschfeld (15E) discusses all of the above terms as well as problems of qualification, quantitation, quantity of sample, spatial and temporal non-uniformity of the sample etc. using simple illuminating models.

Szydlowski (30E) compared a modified AOAC fluorometric method and flameless AA for the analysis of Se in corn oil based infant formulae. For the AA procedure, matrix interferences were minimized by a wet digestion/solvent extraction method. Recoveries for both techniques were 100% and results agreed within experimental error. Kuentz, et. al. (19E) analyzed maple syrup for trace mineral content by dry ashing AA and simple dilution AA methods and found such high variation within replicates that neither procedure was acceptable. Timoshenko, et. al. (31E) compared flame ($N_2O-C_2H_2$) AA and photometric methods for Ca in steels and found no difference between techniques.

Beufays and Nagniot (1E) used differential pulse polarography and AA for the analysis of Cd in water, fertilizer and plant digests finding equivalent results for both.

Optimization. Heineman (13E) discusses the influence of viscosity, temperature, salt content, and surface tension on the efficiency of the AA determination of noble metals and optimizes these and other parameters (12E) using minimum standard deviation as the criterion. Lange (20E) used factorial analysis to identify and minimize interferences (specifically oxide formation) in the analysis of glass. Krasel'shehik and Shteinberg (18E) optimize conditions by defining a parameter proportional to the sum of departures of individual response parameters (signal sensitivity, noise, etc.) from ideality (noise = 0, sensitivity = maximum etc.). Thus, only a single parameter needs to be optimized. Magyar and Widmen (22E) develop an equation which predicts the initial slope of a calibration curve for AA based on such parameters as lamp current, spectral bandpass, and construction and temperature of the atom reservoir. Garnys and Smythe (9E) analyzed lead in whole blood by direct deposition of the blood into a graphite cup atomizer. They found that addition of HNO_3 minimized non-specific absorption and found ash remaining in the cup after a $1700^\circ C$ firing. Some of the ash (which caused a decay in signal as it built up) could be removed using a pipecleaner followed by a $2200^\circ C$ firing.

Raikhbaum, et, al. (29E) developed an empirical equation for generating absorbance vs concentration curves which includes atom transfer, evaporation rate, and atom loss rate terms. Henrion and Raguse (14E) used Cr as an internal standard for Ag analysis by flamephotometry. The Cr was also used to aid in optimizing flame and sample solution properties. Error was reduced 500%.

Development in Technique and Procedure

Elimination, Discussion and Discovery of Interferences

Dawson and Keir (40F) reviewed the various types of interferences most prevalent in flameless atomic absorption, arc, spark, and flame spectrometry. Volke (149F) describes a procedure for preparing calibration curves for Na and K which take into account their mutual interferences. A programmable calculator can then be used to determine the correct concentrations.

Spectral interferences were investigated in detail by Daidohji (39F). Flame emission, molecular absorption and atomic absorption spectra were recorded for the 200 to 400 nm spectral region. Siertsema (140F) found that the uv spectrum of NaCl present in the flame pour serum samples was strongly enhanced by HCl and trichloroacetic acid. Haraguchi, et. al. (60F) found HCl, HBr and HClO_4 interfere with In determinations by flame AA. The cause was formation of diatomic indium halides. They (60.5F) also found that indium oxide shows molecular absorption occurring via photodissociation in the flame. Further studies by these investigators (157F) showed molecular absorption spectra from SrCl or SrBr dissociation in the flame. Massmann, et. al. (97F) show that if the molecular absorption spectrum and the spectral transmission profile of the monochromator are known, reasonable corrections for background structure can be made.

Lovett, et. al. (94F) discuss problems associated with spectral overlap in atomic absorption including direct spectral overlap, multiple absorbing lines in the bandpass, flame emission, molecular absorption etc. Panday and Ganguly (122F) have reported the spectral overlap of Tb/Mg lines (285.21nm) and Cr/Os lines (290.91 nm). Maruta and Sudoh (96F) used the partial overlap of Ge and Ca (422.7nm) to analyze Ca in cements (Ge hollow cathode) without having to make excessive dilutions. Cresser (35F) reviews interference effects in flame AA and notes that interpolation of reported results of incomplete studies is a source of error. Jedrzejewska and Malusecka (72F) found that carriers often used in coprecipitation preconcentration procedures (Fe, La, Fe) do not interfere with Cr, Mn, Sb a Fe determinations if the precipitate is dissolved in HCl but do depress signals in H_2SO_4 . Cresser and McLeod (38F) also find that SO_4^{2-} interferes with Mg, Co and Ni.

Helson and Hermans (65F) find an interelement effect of Cu on Ni. In lean flames Cu enhances the signal in rich flames it is a suppressant. Fujiwara, et. al. find that certain ligands (CN^- , EDTA, oxalate) interfere with first row transition metals in a fuel rich flame but not in a lean flame (49F). The valence of Cr is reported to strongly affect results. Three investigations (26F, 88F, 37F) find that Cr (III) is more sensitive than Cr (VI). It was also shown (88F) that an air/ C_2H_2 flame is more sensitive for Cr than $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ but that the latter is less affected by the Cr valence. In acetone containing solutions, the signal for $\text{Cr}_2\text{O}_7^{2-}$ is dependent on the acetone content the signals for $\text{Cr}_2\text{O}_4^{2-}$ or Cr (III) are not (26F). The effects of Fe, Al, Si, Ca, Mg, Mn, K, Na, HCl, HClO_4 , HNO_3 , HOAc, NH_4OAc and BaCl_2 on the determination of Cr in soils by AA were determined. For the air/ C_2H_2 flame, acids $< 1\text{M}$ did not interfere, in $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ flames only K, Na, BaCl_2 and HOAc interfere (25F). Fuel rich flames were found to minimize the effects. Oguro (117F) studied the effects of ammonium halides on 16 elements finding several substantial interferences. The postulated cause in reactions occurring in cooler flame regions. Park (123F) reports mutual interferences of alkali and alkaline earth elements in their determination in silicates. He finds the effects become nearly constant at high interferent concentration and recommends addition of large excesses to samples and standards. Cioni, et. al. (32F) found that interferences in the determination of Ba in silicates was so severe ion exchange separation was mandatory. Musil and Nehasilova (109F) report numerous interferences in the determination of Si in the $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ flame (Ti, Al, Alkali metals enhance, H_2SO_4 , V, Fe, Ni, Mn suppress). Ostroumenko and Eremenko (120F) find dramatic suppression of Co and Fe by H_2SO_4 and H_3PO_4 in air C_2H_2 flames. The effects are independent of flame temperature by strongly dependent on C_2H_2 implying metal carbide formation. Sebor and Lang (135F) found that analyses for V in petroleum/xylene solutions were unaffected by < 400 ppm I, Br or Cl.

Ammonium perchlorate was found to enhance the signal of several elements. Oguro found that it enhanced Yb (118F), Cr (114F) and Eu (113F) signals and eliminated all interferences except Al, Na, H_2SO_4 and H_3PO_4 for the flame AA analysis. All interferences except Al (were eliminated in the flame emission analysis of Yb (115F) and Eu (116F). Numerous action interferences were found in the AA analysis of V (125F). All but those of Ti were eliminated by addition

of 1mg/mL Al. The interference of various metals in Co based alloys on the AA determination of W were minimized by making solutions and standards 2% Na_2SO_4 (44F).

Kodama, et. al. (86F) found a 120% enhancement of the AA signal for Cr when sodium dodecyl sulfate was added. The signal increased linearly with dodecyl sulfate concentration until the critical micelle concentration was reached. Nicolas and Jones (112F) found dithiocarbamate to eliminate interelement interferences when determining noble metals by AA. Heineman performed a series of noble metal interference studies and found Rh interferes with Pd, Rh does not (61F); Pd and Rh interfere with Pt (62F); and Pd and Pt interfere with Rh (63F). Depending on conditions La, U or Ca are sometimes effective as buffers.

Sample preparation and handling. Holak (67F) describes a temperature programmable furnace for ashing food samples with minimal volatility losses. Tsutsumi, et. al. (143F) ashed cereals at 490°C in glass then added acid to solubilize the ash, extracted into MIBK and analyzed. Wiercinski and Szewczuk (151F) compared wet and dry ashing, freeze drying and simple dilution of bovine serum for Cu, Zn and Fe analyses. The dry ash gave unacceptably low results. Meyer and Meyer (100F) found that while dry ashing bovine liver in porcelain crucibles, Ca was leached from the crucible. Wuyts, et. al. (155F) found that Cu is also leached from porcelain crucibles but Zn is not. Nicholson (111F) used a dry ash procedure with a gold collector for analyses of Hg in rocks, soils and sediments. Koirtzmann and Hopkins (87F) (in a clear case of discrimination) fed adult male rats radiotracers then sacrificed and analyzed them. There were no losses on drying, no volatility losses at $\leq 600^\circ\text{C}$ and only Cr was volatilized from blood at 700°C. Upon dissolution of the ash in acid, however, a significant amount of radiotracer remained in/on the crucible. Menden, et. al. (99F) used rat pups for a dry ashing procedure (300°C for 5 hours, 400°C for 24 hours) then compared various ash dissolutions procedures utilizing aqua regia and sequential HCl, HNO_3 addition. They found no difference in the dissolution procedures. Michette, et. al. (101F) found that low temperature ashing altered the form of some salts and minerals (e.g. partial oxidation of FeS) but not for most.

Jackwerth and Messerschmidt (69F) only partially dissolved Ga samples in HCl/HNO_3 . Elements more noble than Ga remain in or are rereduced onto the Ga (e.g. Ag, Au, Bi, Co, Cu, Fe, Hg, Ni, Pb, Pd, Sn). When ca. 5 mg of Ga is left it is removed and dissolved yielding up to 1000 fold preconcentration of traces.

Delves (41F) added $(\text{NH}_4)_3\text{PO}_4$ to blood and then analyzed the blood for Cd

using the Delves cup. The NH_4 aided in removing NaCl and the PO_4 retained the Cd sufficiently so the Cd absorption peak was separated from the background absorption. Wiercenski (150F) compared 10 methods of serum preparation from simple dilution to dry ashing. The highest readings for Ca and Mg were from a simple trichloroacetic acid denaturization. The lowest Ca value was for simple dilution the lowest Mg for samples 0.1 M in HCl.

Eggimann and Betzer (45F) used sealed teflon bombs and a $\text{HCl}:\text{HNO}_3:\text{HF}$ (15:5:1) acid mix for decomposition of refractory material suspended in sea water. Since boric acid was not necessary, blanks were low as were interferences for non-flame AA determinations.

Assarian and Oberleas (10F) found that the washing procedure followed for hair samples drastically affects the results obtained. A detergent wash removed most Mg and Zn, Hexane/ETOH lowered Mg, and acetone/diethyl ketone/detergent removed Cu.

Barredo and Diez (11F) found that silicate rock fused in $\text{LiCO}_3/\text{H}_3\text{BO}_3$, dissolved in HNO_3 , complexed with EDTA and run gave satisfactory results with no buffers or releasing agents necessary.

Ghiglione, et. al. (51F) use a water immersed spark to generate colloid-like suspensions of metals which may then be used for analysis by AA. The method is rapid (ca 2 min) and the suspensions stable for a few hours.

Zasoski and Buran (158F) find HNO_3 (overnight), heated for 1 hour then HClO_4 added and heated at 200°C until fuming stops is satisfactory for plant and animal tissue digestion. McHand, et. al. (98F) added HNO_3 to frozen orange juice concentrate and determined Ca without needing La to remove PO_4 .

Musil and Dolezal (108F) compared mineral acids and combinations for wet digestions of NBS orchard leaves. HNO_3 or $\text{H}_2\text{SO}_4/\text{HNO}_3$ were best.

Chapman and Dale (31F) reacted Band Si samples with CuOHF forming volatile fluorides for direct injection into a flame for emission (B) or absorption (Si) analysis.

Gladney and Apt (52F) found Ir solutions to be unstable. Os and Ru are much less prone to decomposition.

Extraction Procedures. A comprehensive review of extraction techniques used for atomic absorption and emission has been published by Kuzmin, et. al. (90F). The effects of solvents used for extractions are discussed by Kim (83F). Surfactants (anionic, cationic and non-ionic) were found to have little effect on ammonium pyrrolidine dithiocarbamate extractions (APDC) into MIBK methyl isobutyl ketone (121F). The same extraction system was utilized for heavy metal determinations in plant tissue digest (130F). Agemian and Chau (1F)

compared EDTA, HCl, HNO_3 , $\text{HNO}_3 + \text{HClO}_4$, $\text{HCl} + \text{HNO}_3$ and HF, HNO_3 , HClO_4 as extraction media for trace metal leaching from lake sediments.

Berndt and Jackwerth (21F) formed phenanthroline complexes of trace metals in Mn and Mn compounds. These chelate complexes were coprecipitated with AgI which was filtered and leached with HNO_3 . Mn did not complex and was not precipitated. Berndt, et. al. (22F) also formed complexes with potassium xanthogenate in high Mn containing solutions. Again, Mn does not complex. The complexes were removed by slurrying the solution with activated charcoal and filtering. The charcoal was leached with HNO_3 . Jackwerth and Wilmer (70F) analyzed Cu salts by first eliminating the matrix by precipitation as CuS from sample solutions 3M in HCl. The precipitate was boiled in HNO_3 and the diluted HNO_3 solution analyzed. Bately, et. al. (13F) electrodeposited heavy metals onto pyrolytically coated graphite tubes which were then used for furnace AA. Lund, et. al. (95F) electrodeposited trace metals onto a Pt wire which was then inserted into an air/ C_2H_2 flame for AA analysis.

Other extraction methods are listed in Table II.

AA as a chromatography detector. The specificity of AA makes it attractive as a chromatography detector for chelates and organometallics. Fernandez (46F) reviews both gas and liquid chromatographic applications of AA, particularly for the usefulness of these techniques for speciation studies. Van Loon and Radzuik (148F) describe a quartz atomization cell for such GC/AA studies. These authors (126F) also have used GC/AA for analysis of alkyl selenium compounds. Wolf (152F, 153F) discusses the determination of chromium fluoroacetylacetonates by GC/AA (flame). Parris, et. al. (124F) used GC/AA for the analysis of methylated As, Se and Sn compounds. Chan, et. al. (29F) have developed a GC/AA procedure of tetraalkyl lead compounds. A silica furnace atomizer is used. Robinson, et. al. (127F) discuss the atomization processes for alkyl lead compounds in furnace atomizers. Van Loon, et. al. (147F) describe the use of a non-dispersive AF spectrometric technique for chromatography and discuss the multielement capabilities of the system.

Botre, et. al. (24F) used high performance liquid chromatography (HPLC/AA) for the determination of lead alkyls in gasoline. Jones and Manahan (75F) discuss the HPLC/AA determination of copper chelates of aminocarboxylic acids (EDTA, NTA, EGTA, CDTA) and the detection limits to be expected for the procedure (74F). Jones, Tung and Manahan (76F) demonstrate that the mobile phase used in HPLC/AA may affect nebulization efficiencies, flame temperatures and flame reduction characteristics.

Indirect determinations. The determination of non-metallic species by various indirect methods are summarized in Table III.

Other Techniques and Procedures

Hannaford and Lowe (56F) determined boron isotopic ratios using Ne filled electrodeless discharge lamps as sources for the AA analysis. They found that a sputtering cell was superior to a N_2O/C_2H_2 flame for the analysis. Chapman and Dale (30F) used a dual beam AA for Li isotope analysis. One beam was a 6Li enriched hollow cathode while the other contained Li isotopes in natural abundances. Heilig (64F) published an extensive bibliography of experimentally determined isotope shifts.

Fowler and Winefordner (48F) investigated the background fluorescence spectra obtained using an EIMAC Xe arc continuum source for AFS. Even using an Ar separated air/ C_2H_2 flame backgrounds were high unless precautions were taken (e.g. removal of PH_3 from the C_2H_2).

Omenetto, et. al. (119F) presented a theoretical discussion of what advantages pulsed vs. continuous wave source AFS may have (if any). They conclude that a

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BIENNIAL REVIEW ON FLAME EMISSION, ATOMIC ABSORPTION, AND ATOMI--ETC(U)

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slight advantage may be realized if the system is optimized. Johnson, et. al. (73F) find that due to source instability a pulsed EIMAC offers no improvement over the same source in the CW mode. Haarsma, et. al. (55F) found that HClO_4 added to surface water samples reduced the scattering in flame AFS for Cd and Zn. Scattering was too severe to permit analysis of Cd in sea water. Hannaford and Lowe (57F) found experimental evidence for rare gas quenching in AF. Campeil, et. al. (27F) describe a non-dispersive AF system for the analysis of Hg.

Molecular emission cavity analysis has been quite useful in the analyses of both organic and inorganic moieties. Two useful reviews of the technique have appeared (16F, 20F). Alder, et. al. (8F) have determined S in oils and fuels by charring the oil with sodium metal, dissolving the residue in acid and sweeping the evolved H_2S into an Ar/H_2 flame. Al-Abachi, et. al. (5F) have simultaneously determined mixtures of S containing anions. Belcher, et. al. (15F) determined Cd in an $\text{air}/\text{H}_2/\text{N}_2$ flame using either a carbon or stainless steel cavity. Anionic interferences were removed by addition of H_2SO_4 but Fe, Cr, Mg and Sn interfered. Belcher, et. al. (17F) recorded spectra of several metal halides in a stainless cavity but found all (except Cd) were too weak to be analytically useful in most instances. Narine, et. al. (110F) determined chlorinated pesticides by decomposing the pesticide in an oxygen flask and trapping the evolved HCl. The HCl solution was palced in an In lined cavity and the InCl intensity monitored. Akpofure, et. al. (4F). determined inorganic and organic tin compounds using SnO emission in the cavity. Al-Abachi et. al. (6F) analyzed carbonyl compounds by addition of SO_3^{-2} to the sample. The addition compounds formed unit later than free SO_3^{-2} in the flame. The molecular fluorescence (59F) and molecular absorption (58F) of PO in flames has been measured. The PO absorption band at 246 nm was used to determine P in nucleotides. Henrion, et. al. (66F) analyzed halohydrocarbons by monitoring a CuCl band at 437 nm. Linton and Broida (92F) measured the flame chemiluminescence of T_iO induced by N_2O , NO, NO_2 , CO_2 and O_2 . They also measured the laser induced photoluminescence of T_iO (93F) using dye and Ar-ion lasers. Schanker, et. al. (137F) measured the chmilunescient spectrum of S_iO in flames. The S_iO was formed form SiCl_4 and O atoms.

Belcher, et. al. (19F) used candoluminescent emissions in an $\text{air}/\text{H}_2/\text{N}_2$ flame for the analysis of Eu and Ce. The emissions were activated by an acidified $\text{CaO}-\text{CaSO}_4$ matrix. They found that enhanced sensitivites were obtained if the sample and matrix were heated in the flame (20 to 40s), removed then re-inserted

for analysis. Belcher, et. al. (18F) determined Mn in an air/H₂/N₂ flame. The CaO-CaSO₄ matrix was packed into the heads of Allene screws, sample solutions spotted on the activator, and the screw inserted into the flame. Transition metals interfere and Cl⁻ enhances the emission. Corredor and White (34F) utilized the candoluminescence of Tb⁺³ in silicate, borate, and phosphate glasses for Tb analyses.

Table 1
Measurement of Atomic Excited-State Lifetimes

<u>Element</u>	<u>References</u>
Al	58B
Ba	31B
Bi	69B
Ca	57B
Co	36B
Cs	20B
Fe	36B
Ga	32B, 58B
In	31B, 58B
K	20B
Mg	57B, 172B
Mn	81B
Na	40B
Pb	81B
Rb	20B
Sb	70B
Sm	14B
Sr	31B, 56B, 57B
Tl	58B, 152B

Table II. Extraction Methods

Metals Determined	Extraction Reagent	Solvent	Method	Reference
Ag, Au	phenyl thiourea	MIBK, butanol+chloroform	flame AA	14F
Ag	dithizone	ethylnitrate	flame AA	85F
Ag, Cu, Tl	diphenylthiourea	chloroform	flame AA	141F
Au	ion-exchange	acetone/HCl	flame AA	136F
As(III)	APDC pH 4-6	nitrobenzene	flame AA	156F
As(V) + As(II)	APDC (1M HCl)	nitrobenzene	flame AA	156F
As, Cd, Cu, Sb, Se	comparison of several systems		flame AA	28F
As, Cr, Pb	Zr(OH) ₃	coprecipitation	flameless AA	134F
Cd, Cu, Pb	KI	MIBK	flame AA	144F
Cd, Cu, Mn, Pb, Zn	ion exchange	HNO ₃	flame AA	133F
Cd	dithizone	chloroform	flameless AA	145F
Cd, Co, Cu, Ni, Zn	dithizone	chloroform	flame AA	9F
Cd	dipivaloyl-methane	MIBK	flameless AA	91F
Co	nitrosonaphtol	coprecipitation, MIBK	flame AA	107F
Co	NH ₄ SCN	MIBK	flame AA	23F
Cu, In, Fe, Sn	tri-n-acetylamine (5M HCl)	benzene	flame AA	42F
Cr(VI), Cr(III + VI)	anion exchange resin		flame AA	36F
Hg	MnO ₂ (solid)	trapped Hg from air	cold vapor AA	71F
Mo, Re, W	alkyl amines	chloroform	flame AA	84F
Mn	diethyldithiocarbamate	MIBK	flame AA	138F
Mn	SCN ⁻ , trioctylmethylammonium benzylxanthate	ethyl acetate	flame AA	53F
Mn		MIBK	flame AA	2F
Nb, Ta	HF, H ₂ SO ₄	MIBK	flame AA	89F
Pb	4-benzoyl-3-methyl-1-phenyl-5-pyrazolone	MIBK	flame AA	3F
Sb			flame AA	146F
Te	coprecipitation with As(0)		flame AA	54F
W	SCN ⁻	MIBK	flame AA	108F
Zn	activated charcoal	HCl	flame AA	142F

Table III. Indirect Determinations

Species Determined	Procedure	Reference
F ⁻	monitor F ⁻ interference on Mg ⁺² as function of pH	47F
S	oxidize S in plant tissue to SO ₄ ⁻² , precipitate BaSO ₄ , measure Ba ⁺⁴	12F
SO ₄ ⁻²	precipitate BaSO ₄ , measure Ba ⁺⁺	50F
SO ₄ ⁻²	precipitate PbSO ₄ , filter into carbon cup, use furnace AA for Pb	139F
Biuret	in strong base Cu forms a biuret complex. Filter off Cu(OH) ₂ measure Cu	154F
Biuret	a comparison of Cu/AA procedure with AOAC methods	33F
Folic acid	oxidize with KMnO ₄ complex product with Ni, extract into MIBK	80F
Amino acids	form Schiff bases, complex with Cu, extract	82F
Histidine/methionine	Schiff bases, Cu complex	81F
benzylpenicillin	ion pair with Cd-1,10-phenanthroline complex, extract	79F
CN ⁻	filter sample (neutral) through CuCN, get Cu(CN) ₂ complex	77F
F (in fluoro organics)	decompose with sodium biphenyl add Fe(SCN) ₆ ⁻³ extract excess Fe with MIBK	78F
noscapine	add Reinecke's salt, extract, measure Cr	102F
aldehydes	add Tollen's reagent, measure Ag	104F
nitro compounds	reduce with Zn dust, add Tollen's reagent to resulting hydroxylamine solution	106F
alcohols	add CrI ₃ and pyridine to benzene solution, measure Cr in solution	105F
polyhydric alcohols	add HIO ₄ , precipitate IO ₃ ⁻ with Ag, measure Ag in solution	103F
germanium	form molybdo-germanic acid, extract, determine Mo	128F
quarternary amines	complex with excess dioctylsulfon-succinate, extract that remaining as Cu orthophenanthroline complex, measure Cu in extract	7F

Table III (Continued)

Species Determined	Procedure	Reference
CS_2	trap in KOH, remove H_2S with Cd, form Cu xanthate	129F
P	form molybdophosphoric acid, extract, determine Mo	68F
SO_4^{-2}	titrate with Ca, measure inhibition of Ca signal	131F
SiO_4^{-2} , PO_4^{-3} , SO_4^{-2}	Ca inhibition titration	132F

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